Atmos. Chem. Phys. Discuss., 14, 32709–32933, 2014
www.atmos-chem-phys-discuss.net/14/32709/2014/
doi:10.5194/acpd-14-32709-2014

Atmospheric Chemistry and Physics
Discussions
Open Access

Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer

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Received: 7 November 2014 – Accepted: 14 November 2014 – Published: 22 December 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Ozone holds a certain fascination in atmospheric science. It is ubiquitous in the atmosphere, central to tropospheric oxidation chemistry, yet harmful to human and ecosystem health as well as being an important greenhouse gas. It is not emitted into the atmosphere but is a by-product of the very oxidation chemistry it largely initiates. Much effort is focussed on the reduction of surface levels of ozone owing to its health impacts but recent efforts to achieve reductions in exposure at a country scale have proved difficult to achieve due to increases in background ozone at the zonal hemispheric scale. There is also a growing realisation that the role of ozone as a short-lived climate pollutant could be important in integrated air quality climate-change mitigation. This review examines current understanding of the processes regulating tropospheric ozone at global to local scales from both measurements and models. It takes the view that knowledge across the scales is important for dealing with air quality and climate change in a synergistic manner.

1 Introduction

Ozone is central to the chemistry of the troposphere owing to its role in the initiation of photochemical oxidation processes via direct reaction, photolysis and the subsequent reactions of the photoproducts to form the hydroxyl radical (Monks, 2005). Tropospheric ozone is also recognised to be a threat to human health (WHO, 2003; Lim et al., 2012), to have a deleterious impact on vegetation (Fowler et al., 2009) and, through plant damage it impedes the uptake of carbon into the biosphere (Sitch et al., 2007). It is also an important tropospheric greenhouse gas (IPCC, 2007; Stevenson et al., 2013) and is referred to as a short-lived climate pollutant (Shindell et al., 2012).

Ozone-related deaths are estimated to make up about 5–20 % of all those related to air pollution e.g. (Silva et al., 2013; Anenberg et al., 2009; Lim et al., 2012; Brauer et al., 2012). The OECD (OECD, 2012) have stated that “without new policies, by 2050, air pollution is set to become the world's top environmental cause of premature mortality." The report goes on to state that "Because of their ageing and urbanised populations, OECD countries are likely to have one of the highest premature death rates from ground-level ozone".

While ozone has a relatively short atmospheric lifetime, typically hours, in polluted urban regions where concentrations of its precursors are high, its lifetime in the free troposphere is of the order of several weeks (Stevenson et al., 2006; Young et al., 2013), sufficiently long for it to be transported over intercontinental scales. Thus, in addition to its role as a priority pollutant on an urban scale, it may influence air quality on a hemispheric scale (Akimoto, 2003; HTAP, 2010). There is little doubt that ozone is a multifarious molecule. Recently, Simpson et al. (2014) described ozone as the persistent menace. Figure 1 shows some of the key interactions that drive ozone concentrations in the troposphere and some of the feedbacks.

Historically, tropospheric ozone was thought to be rather unimportant in atmospheric chemistry terms, being controlled by its main source in the stratosphere and subsequently transported by synoptic scale subsidence and turbulent mixing to the surface, where it is destroyed (Junge, 1962). If tropospheric ozone photochemistry was important at all, then this was limited to highly polluted locations such as to the Los Angeles basin (Leighton, 1961). On this basis, long-range transport appeared to be the dominant process with the tropospheric ozone budget controlled by stratosphere–troposphere exchange and surface destruction. The spring-time ozone maximum which occurred simultaneously with the annual influx of radioactive tracers from the stratosphere, confirmed the importance of transport processes. Crutzen (1973) proposed the contrary position that photochemical ozone production involving hydrocarbons and oxides of nitrogen may take place throughout the unpolluted troposphere. Furthermore, Chameides and Walker (1973) suggested that ozone in the lower troposphere was entirely controlled by atmospheric chemistry. These latter suggestions were strongly contested (Chatfield and Harrison, 1976; Fabian and Pruchniewicz, 1977) and have been the subject of much debate over the intervening years (Monks, 2000).

This review examines current understanding of the processes regulating tropospheric ozone at global to local scales from both measurements and models. It takes the view that knowledge across the scales is important for dealing with air quality and climate change in a synergistic manner. It would be a herculean task to review all the literature on ozone, therefore much of the focus of this review is on the recent findings and discoveries relating to tropospheric ozone. It builds on earlier integrative reviews such as Brasseur et al. (2003) and the ACCENT reviews (Fowler et al., 2009; Isaksen et al., 2009; Monks et al., 2009; Laj et al., 2009).

The review has four major sections. The first reviews the control of ozone across the scales, looking at the interplay of chemistry, transport and deposition, and includes a brief climatological picture of ozone. The second major section details the major impact of ozone with respect to health, ecosystems and climate, while the third section highlights several current topics in relation to ozone in the troposphere. The final section briefly overviews some of the policy context and issues in relation to tropospheric ozone. In the conclusion, some future directions and issues with relation to ozone are discussed.

2 Ozone – control, precursors and climatology

2.1 What controls ozone?

The annual variation in ozone concentration at any given spatial scale depends on a number of factors, such as the proximity to large sources of ozone precursors, geographical location and the prevailing meteorological conditions (Logan, 1985). The tropospheric ozone budget at a given location is dependent on both photochemical processes and physical processes, including photochemical production and destruction of ozone, transport from upwind sources and removal at the Earth's surface (Monks, 2000; Lelieveld and Dentener, 2000).

Given the substantial stratospheric ozone concentrations, transport from the stratosphere was long thought to be the dominant source of ozone in the troposphere (Danielsen, 1968; Junge, 1962; Fabian and Pruchniewicz, 1977). Photochemical mechanisms for the generation of ozone were first identified in work carried out in California in the 1950s (Haagen-Smit, 1952) and until the 1970's high ozone was thought to be a local phenomenon associated with air pollution. Early in the 1970's Crutzen (1973) and Chameides and Walker (1973) suggested that tropospheric ozone originated mainly from production within the troposphere by photochemical oxidation of CO and hydrocarbons catalysed by HO_x and NO_x. Since then, improved understanding of the importance of both natural and anthropogenic sources of ozone precursors has highlighted the dominance of this ozone source, and recent model assessments suggest that chemical production contributes about 5000 $Tg\,yr^{-1}$ to global tropospheric ozone (Stevenson et al., 2006; Young et al., 2013). In contrast, the net global source of ozone from stratosphere–troposphere exchange (STE) is estimated to be about 550 $Tg\,yr^{-1}$ based on observational constraints (Olson et al., 2001; McLinden et al., 2000). The removal of ozone through dry deposition to vegetation and other surfaces at ground level remains poorly constrained on the global scale, although model assessments driven by observed ecosystem fluxes, vegetation types and meteorology suggest net removal of about 1000 $Tg\,yr^{-1}$ (Stevenson et al., 2006). Balancing the global tropospheric ozone budget therefore requires that there is net chemical production of about 450 $Tg\,yr^{-1}$ (Stevenson et al., 2006). Note that this term is constrained by the estimated STE and deposition terms and by the global tropospheric ozone burden of about 335 Tg, and that uncertainty in the absolute magnitude of gross ozone chemical production and destruction remains relatively large (Wild, 2007).

These global budgets mask substantial regional variation (see Fig. 2) which spans the wide range of chemical environments present in the troposphere. Troposphere-wide chemical production of ozone from long-lived hydrocarbons such as methane is greatest in the tropical lower troposphere where OH radical concentrations are high (Bloss et al., 2005), and in continental regions and parts of the free troposphere with fresh NO_x emissions. Chemical destruction of ozone is largest in the lower troposphere where water vapour concentrations are high and in highly polluted regions where there is direct removal by reaction with NO. This latter condition is commonly referred to as chemical titration of ozone, and is typically short-lived as the NO_2 formed subsequently catalyses further ozone formation once it has been transported into cleaner environments. Localised halogen-catalysed ozone destruction may also affect surface ozone in polar-regions during spring time (see Halogens section). Consequently, net chemical production occurs over most of the continental boundary layer where precursor concentrations are high and in the upper troposphere, where destruction is slow (Wild and Palmer, 2008; von Kuhlmann et al., 2003a, b). Net chemical destruction occurs in the mid-troposphere and marine boundary layer where precursor concentrations are low and in localised urban and Polar Regions under *titration* (via reaction with NO) and halogen destruction conditions, respectively. Despite large changes in the emissions of ozone precursors and in net chemical production, the general location of these net production and loss regimes is thought to have changed little since preindustrial times (Wild and Palmer, 2008). However, spatial heterogeneity of anthropogenic precursor emissions and of biogenic hydrocarbons (Zare et al., 2014), along with strong diurnal variability in chemical processes, deposition and meteorology, suggests that local ozone production and loss regimes in the boundary layer may be much more diverse than indicated by these coarse regional-scale assessments.

2.1.1 Role of chemistry

The basic chemistry that leads to the production and destruction of ozone has been detailed elsewhere (Monks, 2005; Ehhalt, 1999; Jenkin and Clemitshaw, 2000). Ozone (O_3) photochemical production in the troposphere occurs by hydroxyl radical oxidation of carbon monoxide (CO), methane (CH_4), and non-methane hydrocarbons (generally referred to as NMHC) in the presence of nitrogen oxides (NO_x). The mechanism of ozone formation in the troposphere, although very well understood, remains a challenge that will, no doubt, require many more years of research to fully unravel. In brief, the production of ozone in the troposphere relies, fundamentally, on the photolysis of NO_2 (Reaction R1) and the subsequent association of the photoproduct $O(^3P)$ (the ground electronic state oxygen atom) with O_2 via Reaction (R2) through a termolecular reaction with a third body (M being used to represent any third co-reactant i.e. N_2):

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{R1}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{R2}$$

The difficulty with understanding the production of O_3 in the troposphere comes about through the manifold ways in which NO and NO_2 are interconverted. The rapid interconversion between the two compounds allows them to be treated as a chemical family – NO_x. (NB photolysis of NO_2 is fast, and approximately altitude independent – $j_1 \approx 10^{-2}\,s^{-1}$). For example, the reactions

$$HO_2 + NO \rightarrow NO_2 + OH \tag{R3}$$

$$O_3 + NO \rightarrow NO_2 + O_2, \tag{R4}$$

both convert NO into NO_2. Considering Reactions (R1), (R2) and (R4) one can derive a ratio of $[NO]/[NO_2]$ that depends on the local concentration of O_3 and the rate coefficients for Reaction (R4) and the photolysis frequency for Reaction (R1) (at the surface the pseudo first order rate constant k_2' ($k_2 \times [O_2] \times [M]$) is sufficiently fast that it is not a rate limiting step). This ratio is termed the Leighton ratio (Leighton, 1961) and also allows for an expression to be derived for the equilibrium concentration of O_3. Whilst this chemistry is important, particularly in urban areas, it does not represent a mechanism for the net production of O_3 in the troposphere. Considering the addition of volatile organic compounds, such as CO:

$$CO + OH(+O_2) \rightarrow CO_2 + HO_2 \tag{R5}$$

We are able to write a mechanism for the formation of O_3 that is propagated via VOC and NO_x (Reactions R5, R3, R2 and R1). In this series of reactions O_3 is used as a source of the hydroxyl radical (OH) through:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{R6}$$

$$O(^1D) + H_2O \rightarrow OH + OH, \tag{R7}$$

where $O(^1D)$ is the electronic excited state atomic oxygen formed through photolysis at wavelengths < 320 nm. However, the presence of VOC (CO) and NO_x, allow OH to be regenerated and promote formation of O_3 through NO_2 photolysis. The production of O_3 in the troposphere, mediated through the reactions involving VOC and NO_x is shown schematically in Fig. 3.

Figure 3 highlights the non-linearity of the O_3-VOC-NO_x system. The O_3 mixing ratios presented in Fig. 3 are generated from photo-chemical modelling output generated using the UKCA model (O'Connor et al., 2014; Archibald et al., 2011). Regions in Fig. 3 where there is net O_3 destruction (top left and bottom right corners) are typically referred to as the VOC limited and NO_x limited regimes. VOC limited refers to the fact that the production of O_3 is limited by the input of VOC (see e.g. Zhou et al., 2014). This can be rationalized by moving from point A to point B along a line of constant NO_x emissions and increasing VOC emissions. Moving in this direction it is evident from Fig. 3 that O_3 production increases. A similar case applies for the NO_x limited regime where this time moving from point C to point B requires increasing NO_x emissions and results in increasing O_3 mixing ratios.

This general mechanism of OH initiated O_3 formation can be extended to more complex VOC such as alkanes:

$$C_2H_6 + OH + O_2 \rightarrow C_2H_5O_2 + H_2O \tag{R8}$$

$$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2 \tag{R9}$$

Where $C_2H_5O_2$ represents a member of a group of radicals termed organic peroxy radicals (RO_2 – where R is used to represent alkyl, allyl, or aryl groups), all of which possess the ability to convert NO to NO_2. The fate of the alkyl oxy radical (C_2H_5O) is more complex and can result in the formation of HO_2 and other VOCs. It is the organic atmospheric chemistry of RO_2 that remains the great challenge to our full understanding of the production of O_3 in the troposphere. Recent advances in our understanding of the fate of RO_2 in the atmosphere are reviewed in Sect. 4.10.

There are added complexities to the chemistry outlined above owing to the variety of sources of OH e.g. from the photolysis of HONO (Kim et al., 2014), HCHO and the reaction of ozone with alkenes. The Monks et al. (2009) review looked at much of the variety of ozone photochemistry in more detail.

2.1.2 Role of deposition

The concentration of ozone in the surface boundary layer is regulated by three processes: atmospheric transport, chemical production/destruction and losses to surface by dry deposition. Ozone is physically transported to the surface by atmospheric turbulence which is readily measured or modelled using well established methods. The rate of ozone removal at the surface strongly influences the exposure of vegetation and the human population to ozone and is responsible for much of the nocturnal decline in surface ozone in rural areas as deposition to the surface consumes ozone beneath a nocturnal temperature inversion. During the day, vertical transport of ozone to the surface layers is generally sufficient to maintain mixing ratios within 10 % of the boundary layer mean values, except in urban areas or near major roads, where local nitric oxide sources remove ozone by titration (Colette et al., 2011). Thus the interplay between dry deposition of ozone in the surface layers and mixing from higher levels in the atmosphere plays a major role in regulating ozone exposure of ecosystem and the human population. The mixing in surface layers is largely driven by wind and its interaction with frictional drag at the surface. The large diurnal variability in ozone mixing rations in rural areas and its variability with altitude has been used to quantify the spatial variability in ozone exposure at the surface.

Ozone dry deposition has been widely measured using micrometeorological methods, which average the flux to the surface at the field to landscape scale, over typically (10^4–10^6 m^2) (Fowler et al., 2009). The controlling processes in ozone deposition are generally simulated numerically using a resistance analogy (Erisman et al., 1994), as illustrated in Fig. 4. Correct parameterisation in models is critical to the determination of ozone budgets (Val Martin et al., 2014).

Ozone is a reactive gas and deposits readily on most surfaces simply by oxidative reactions (Grontoft, 2004). Many studies have concluded that stomatal uptake is the main factor regulating surface fluxes, but as stomata are open only a fraction of the time, the smaller rates of deposition to non-stomatal surfaces are often a dominant component of the annual deposition to the surface (Fowler et al., 2009).

Considering the main sinks for ozone deposition at the surface in turn:

a. Stomatal uptake

Plants open their stomata to take up CO_2 for photosynthesis and regulate stomatal opening to minimise water loss by transpiration (Farquhar et al., 1980). This also allows the uptake of other gases that may not benefit the plant, including ozone, which as a powerful oxidant, generates free radicals within the apoplast and cell fluids and is responsible for damage to cell metabolism (Mills et al., 2011). Stomatal opening is controlled by water pressure in the guard cells which the plant regulates depending on: light, in general stomata open during the day and close at night; carbon dioxide concentration; plant water content, to control water loss; temperature, in most conditions an increase in temperature increases stomatal opening. Other factors can affect stomatal opening although not as directly as those listed above: the age of a plant has an influence as older cells become damaged and respond more slowly to stimuli; pollutant gases or aerosols can damage the guard cells or block stomata; surface water blocks stomata.

The diffusion pathway through stomata as with atmospheric fluxes, can be quantified using a resistance analogy as illustrated in Fig. 4. The inverse of stomatal resistance is stomatal conductance (g_s) and is widely used by plant scientists to quantify stomatal exchanges of CO_2 and H_2O. The inverse of the total resistance between a reference height in the atmosphere and the absorbing surfaces is referred to as a deposition velocity (V_d) and is widely used to quantify dry deposition of pollutant gases in transport and deposition models. The processes responsible for controlling stomatal function have been extensively studied in the field and laboratory leading to a variety of instruments and models to quantify stomatal resistance, R_{c1}, or conductance, g_s.

b. Non-stomatal uptake

The reaction of ozone with external surfaces of vegetation is referred to as non-stomatal uptake. In controlled conditions in the laboratory, the flux may be measured quite straightforwardly by treating the vegetation to fully close stomata. In the field, there is the complication that multiple sinks are present (leaf surfaces, senescent vegetation, soil and water). The usual approach to quantify non-stomatal deposition is by the difference between the total deposition flux and the stomatal flux, choosing surfaces to minimise the soil and senescent vegetation components. With reference to Fig. 4, once R_{c1} has been determined from measurements or by modelling the sum of R_{c2}, R_{c3} and R_{c4} (non-stomatal, R_{ns}) can be calculated as the residual term:

$$R_{ns} = \left(\frac{1}{R_c} - \frac{1}{R_{c1}}\right)^{-1} \tag{1}$$

Whether it is possible to separate the components of R_{ns} (R_{c2} – external surfaces, R_{c3} – soil, R_{c4} – in-canopy chemistry) depends on the nature of the measurement site and canopy and there are some models available based on measurements over bare soil, senescent vegetation and in-canopy chemistry (Launiainen et al., 2013; Fares et al., 2013, 2012; Bueker et al., 2012; Tuzet et al., 2011; Stella et al., 2011). Many research groups have taken this approach and Table 1 provides a summary of some of the different estimates of the values for R_{ns} in the literature.

The literature reviewed in Table 1 reports estimates of R_{ns}, although few examine the controlling factors. In some of the studies, surface factors affecting ozone deposition, other than stomatal uptake, have been considered. The main focus of work has been on the effects of surface water and researchers have found both positive and negative effects on deposition rates. The remainder of studies have considered solar radiation or surface temperature and found deposition rates increased with both variables, as well as in-canopy chemistry.

c. Solar radiation and surface temperature

Given its reactive nature it is not unreasonable to find effects of surface temperature on R_{ns} and indications of such an effect were first reported by Rondon et al. (1993). In their measurements of ozone deposition to a coniferous forest they found that the surface resistance to ozone was much lower than that predicted by stomatal conductance alone and the residual term (R_{ns}) varied with air temperature, radiation and stomatal conductance. It was proposed that this effect was due to temperature increasing the reaction rates of ozone with organic compounds on the canopy surface. Coyle et al. (2009) found similar results in measurements for ozone uptake by potatoes, while also showing that surface wetness could enhance or reduce non-stomatal uptake depending on the initial status of the cuticles. Fowler et al. (2001) showed a clear reduction in R_{ns} with increasing total solar radiation and temperature. Cape et al. (2009) examined deposition to metals and artificial leaf surfaces and found a strong temperature response, which yielded activation energies for the reaction of $\sim 30\,\mathrm{kJ\,mol^{-1}}$, similar to that found by Fowler et al. (2001) for moorland of $36\,\mathrm{kJ\,mol^{-1}}$ and from other unpublished studies (Coyle et al., 2009). The simplest explanation of non-stomatal ozone deposition is that it represents the thermal decomposition of ozone at the surface, which increases with surface temperature. Other, more complex processes have been suggested including rapid reactions with very reactive hydrocarbon compounds (Hogg et al., 2007).

d. In-canopy chemistry

The reaction of ozone with nitric oxide (NO) is an important cause of reduced ozone concentrations in urban areas. The same reaction also reduces ozone concentrations close to the surface where soil emissions of NO are large. Some types of vegetation such as coniferous forests also emit highly reactive volatile organic compounds (Di Carlo et al., 2004) which can rapidly deplete ozone concentrations immediately above the canopy (Neirynck et al., 2012; Stjernberg et al., 2012). Over some forest canopies the major non-stomatal sink has been attributed to these reactions although the compound(s) responsible have not been identified. Other transient events such as grass cutting, which releases very reactive hydrocarbons (Davison et al., 2008) can also lead to enhanced ozone deposition as a result (Coyle, 2005).

e. Deposition to water

It has often been assumed that ozone deposition rates will be small and relatively constant as ozone has a low solubility in water. The resistance of a water layer to the uptake of ozone by dissolving and diffusing the gas is very large and values of 3×10^5 to $8 \times 10^5\,\mathrm{s\,m^{-1}}$ have been suggested (Wesely et al., 1981). They concluded that the far lower values found in their measurements (Table 1) resulted from surface chemical reactions, which has been supported by further work since then. However, measurements have shown that over vegetated surfaces deposition can be either enhanced or suppressed by the presence of water films (Fuentes et al., 1992; Padro, 1994; Grantz et al., 1995, 1997; Pleijel et al., 1995; Coyle et al., 2009) while over open water deposition varies with water chemistry, turbidity and agitation. The deposition velocity of ozone to open water is generally small, ~ 0.001 to $0.04\,\mathrm{cm\,s^{-1}}$ (Wesely et al., 1981; Chang et al., 2004) and increases in deposition velocities to sea water have been observed with disturbance to the surface. McKay et al. (1992) showed that increasing concentrations of chemical surfactants in the seawater also enhanced deposition (see Table 1 for typical resistance values). These results show that although deposition rates to water are generally small they can be significant if other reactive compounds are present in the water, a conclusion also supported by measurements to wet vegetated canopies. Research into ozone reactivity and solubility for the ozone water treatment industry has highlighted the role of pH. Ganzeveld et al. have explored the impact of dry deposition of ozone over oceans (Ganzeveld et al., 2009). On a global scale, model studies indicate that deposition to the ocean constitutes almost 40 % of the total annual surface dry deposition of ozone, far larger than that from any other land cover class (Hardacre et al., 2014).

2.1.3 Transport and mixing processes

Long-range transport

Research over the past two decades has clearly shown that ozone and ozone precursors are regularly exported from their emission source, or point of production, to receptor regions far downwind on the regional, intercontinental and even hemispheric scale (see reviews by Stohl and Eckhardt, 2004; Monks et al., 2009; National Research Council, 2009b; HTAP, 2010). These transport pathways are predominantly from west to east at mid-latitudes with in situ and satellite-based observations showing that pollution plumes (anthropogenic and biomass burning) not only travel from North America to Europe, or from East Asia to North America, but can also circle the globe (Jacob et al., 1999; Jaffe et al., 1999; Lewis et al., 2007; Wild et al., 2004).

The scientific community has a very good understanding of the meteorological mechanisms that export pollution from the boundary layer of a source region (warm conveyor belts, deep convection, and horizontal advection) and then transport these plumes through the free troposphere towards the downwind receptor region. The most recent development is the conceptualization of intercontinental transport within an isentropic framework that illustrates how transport of pollution plumes from East Asia are constrained by the thermal structure of the atmosphere, preferentially impacting the high elevation terrain of the western USA rather than the relatively low-lying eastern USA (Brown-Steiner and Hess, 2011). The major uncertainty concerning long-range transport is estimating the contribution of the imported pollution to the total quantity of pollution at the surface of the receptor region. Some unique chemical tracers of upwind pollution sources do exist, for example, stable lead isotopes can indicate events when Asian particulate matter reaches the surface of California (Ewing et al., 2010). However, at present there are no routine and widespread monitoring methods that can distinguish ozone and ozone precursors produced in a receptor region, such as California, from the same species produced in an upwind region, such as East Asia.

The only feasible method for quantifying the impact of imported pollution at the surface of a receptor region is to use chemical transport models or chemistry-climate models. Such models have been used for this purpose since the 1990s but until recently their effectiveness has been limited by their coarse horizontal resolution, typically $2^\circ \times 2^\circ$ (HTAP, 2010). Such large grid cells artificially dilute the imported pollution plumes as well as local emissions of ozone precursors in the receptor region, and also smooth the topography of the receptor region, removing the influence of terrain-driven transport mechanisms that affect the mixing of imported pollution down to the surface. However, recent model studies have used finer scale grids to avoid the problems associated with coarse resolution models (Lin et al., 2012b; Huang et al., 2013; Zhang et al., 2014; Choi et al., 2014). Because these finer resolution models provide more realistic simulations of observed pollution plumes scientists have greater confidence in their quantification of the contribution of imported pollution at the surface of a receptor region. Despite the improvements afforded by finer resolution, a recent study of the quantity of background ozone advected into western North America shows monthly mean differences as great at 10 ppbv between models, with the discrepancy attributed to differences in the way that the models handle lightning NO_x, biogenic isoprene emissions and chemistry, wildfires, and stratosphere-to-troposphere transport (Fiore et al., 2014). Future climate change may affect the contribution of long-range transport downwind effects (Glotfelty et al., 2014; Doherty et al., 2013).

Seasonal transport patterns: stratosphere–troposphere exchange and summer monsoons

The tropospheric ozone burden varies seasonally (e.g. Ziemke et al., 2006). The region of the Earth with the strongest seasonal ozone variation is the northern mid-latitudes where the ozone burden is at a minimum in October and November and then increases by 30 % through winter and spring until it reaches a maximum in June (Cooper et al., 2014). Much of this seasonal variability can be explained by the flux of ozone from the stratosphere to the troposphere with a Northern Hemisphere peak flux in May and a minimum flux in November occurring predominantly in mid-latitudes (Hsu and Prather, 2009). Until recently ozone transport from the stratosphere to the troposphere was believed to be dominated by processes such as tropopause folds and gravity wave breaking, with little attribution given to deep convection (Stohl et al., 2003). However, a new model-based estimate that accounts for deep convection penetrating the lowermost stratosphere increases the Northern Hemisphere peak stratosphere-to-troposphere ozone flux by 19 % and shifts the peak month from May to June (Tang et al., 2011). Sudden STE events are well known to influence ground-based ozone measurements over a short period (see e.g. Dempsey, 2014; Zanis et al., 2003).

While the tropospheric ozone burden responds seasonally to the flux from the stratosphere the response is not uniform with altitude or latitude. Terao et al. (2008) using a chemical transport model calculated the stratospheric contribution to monthly mean ozone above four ozonesonde sites between 75° N and 36° N. At 500 hPa the stratospheric contribution to ozone is ∼ 40 % during spring and 25 % in autumn at high latitudes, and 35–40 % during spring and 10–15 % during autumn at mid latitudes. At 800 hPa these values are slightly less on a percent scale but much less on an absolute scale, being ∼ 20 ppbv during spring and 5–7 ppbv during autumn with relatively little latitudinal gradient. Model estimates of the stratospheric contribution to surface ozone are smaller than those for 800 hPa but the estimates vary greatly depending on the model used and the region under consideration. For example, Lamarque et al. (2005)

estimated that the monthly mean stratospheric contribution to a range of sites in the mid-latitudes and tropics of both hemispheres is always less than 5 ppbv, regardless of season. In contrast, a study using a different model estimated the stratospheric contribution to US surface ozone during late spring 2010 as being < 5 ppbv along the Gulf coast, 8–13 ppbv across the eastern US, and 10–20 ppbv across the high elevations of the western USA (Lin et al., 2012a). More recently Hess et al. (2014) have claimed that that a large portion of the measured ozone change in the sub-tropical NH are not due to changes in emissions, but can be traced to changes in large-scale modes of ozone variability.

In addition to the seasonal influence of stratosphere–troposphere exchange, ozone varies seasonally at most sites around the world (Oltmans et al., 2013) simply due to shifting wind patterns associated with migratory mid-latitude cyclone tracks or the transition between winter and summer monsoons. For example, Mauna Loa Observatory, Hawaii in the northern tropics is influenced by westerly air masses from Asia in the spring when it is located beneath the subtropical jet stream. But in autumn the subtropical jet stream is far to the north leaving the site well within the tropical belt which reduces transport from Asia resulting in 25 % decrease in monthly median ozone (Lin et al., 2014b). Similarly, Bermuda in the subtropical North Atlantic Ocean receives westerly transport from North America during winter and spring, but during summer the westward and northward expansion of the Azores–Bermuda High advects tropical air masses to Bermuda reducing ozone mixing ratios by 50 % (Moody et al., 1995). The North American Summer Monsoon becomes established above central North America during July and August producing a stationary upper tropospheric anticyclone that traps ozone precursors lofted from the surface as well as large quantities of lightning NO_x (Cooper et al., 2009). Over several days the ozone precursors enhance tropospheric ozone within the anticyclone by as much as 30–40 ppbv compared to sites upwind of the anticyclone (Cooper et al., 2007). Ozonesondes launched from Ahmedabad, western India indicate that an upper tropospheric ozone enhancement does not occur during the Asian Summer Monsoon despite the presence of an anticyclonic recirculation similar to that found above North America during its summer monsoon. Instead, an abrupt decrease in tropospheric column ozone is observed above Ahmedabad with the onset of the Asian Summer Monsoon, with decreases occurring at all levels of the troposphere (Ojha et al., 2014).

Climate variability

While mean climatic conditions are typically established over a 30 year period, climate variability occurs on much shorter time scales of one to several years. Short-term climate variability modifies the long-range transport pathways that channel ozone plumes on regional and intercontinental scales, and also impacts regional-scale ozone photochemistry by modifying cloud cover. The impact of climate variability on ozone transport and chemistry is a relatively new field of study that has explored the effects of such phenomena as El Niño/Southern Oscillation (ENSO), the Pacific–North American (PNA) pattern and the North Atlantic Oscillation (NAO).

ENSO has been shown to modulate the tropospheric ozone burden across the tropical Pacific Ocean with lower tropospheric column ozone corresponding to the cloudiest regions (Ziemke and Chandra, 2003; Sekiya and Sudo, 2014). Zeng and Pyle (2005) calculated an anomalously large increase of stratosphere–troposphere exchange following a typical El Niño year, increasing the global tropospheric ozone burden. In addition, changes in emissions, especially biomass burning, associated with ENSO affect the ozone burden across the tropics (Doherty et al., 2006). ENSO has also been linked to column ozone changes above Europe with positive anomalies of tropospheric ozone column and surface ozone occurring in the spring following an El Niño year, for a variety of reasons including changes in STE, biomass burning emissions and pollution transport pathways from Asia and North America (Koumoutsaris et al., 2008). Voulgarakis et al. (2010) used a global chemical transport model to determine the interannual variability of the global tropospheric ozone burden for the period 1996–2000 which included the strong El Niño event of 1997–1998. They found that 79 % of the interannual variability was due to changes in meteorology (mostly stratosphere–troposphere exchange) and only 11 % was due to changes in emissions. Changes in cloudiness contributed a small but non-negligible amount (6 %) to the interannual variability. ENSO and the Pacific–North American (PNA) pattern also control the transport of ozone from East Asia to Mauna Loa, Hawaii. A springtime decrease in transport from Asia to Mauna Loa over the period 1980–2011 has resulted in no significant ozone trend, while an increase in transport during autumn has produced a very strong ozone trend of 3.5 ± 1.4 ppb decade^{-1} (Lin et al., 2014b).

The transport of ozone and other pollutants across the North Atlantic Ocean and the Arctic is heavily influenced by the NAO. During the high phase of the NAO, wintertime pollutant transport into the Arctic is enhanced by 70 % compared to times dominated by the low phase, with the major source region being Europe, followed by North America (Eckhardt et al., 2003). The NAO has also been shown to modulate ozone at the high elevation site of Izaña in the subtropical North Atlantic Ocean (Cuevas et al., 2013), with a relaxation of the predominantly high positive phase of the NAO since the mid-1990s allowing increased ozone transport from North America and the lower stratosphere to Izaña in more recent years. Across Europe surface ozone observations tend to correlate positively with the NAO (Pausata et al., 2012).

While transport of ozone from the stratosphere to the troposphere has a strong seasonal cycle, recent work has also explored changes in the stratosphere-to-troposphere ozone flux and its impact on the tropospheric ozone budget. Several modelling studies have given evidence for such a link (Young et al., 2013; Kawase et al., 2011; Hess and Zbinden, 2013; Voulgarakis et al., 2011; Oman et al., 2013), even demonstrating that the Mount Pinatubo eruption of 1991 reduced the flux of ozone from the stratosphere to the troposphere until 1995 (Tang et al., 2013). According to a model-based analysis, the interannual variability of the ozone mass flux from the stratosphere to the troposphere is on the order of 15 % for the Northern Hemisphere and 6 % for the Southern Hemisphere (Olsen et al., 2013). Correlations between remotely sensed ozone in the lowermost stratosphere and mid-troposphere indicate that 16 % of the Northern Hemisphere mid-latitude tropospheric interannual ozone variability is controlled by the flux from the stratosphere (Neu et al., 2014). Ordoñez et al. (2007) showed that the positive ozone trends and anomalies in the lower free troposphere over Europe during the 1990s were probably due to enhanced stratospheric ozone contributions (dominated by changes in lower stratospheric ozone concentrations rather than by variations of cross-tropopause air mass transport), particularly in winter–spring. Similarly, Tarasick et al. (2005) using the ozonesonde network over Canada, and Terao et al. (2008) using a global model for the northern extratropics found positive correlations between ozone in the troposphere and the lowermost stratosphere. Using the same data as Ordoñez et al. (2007) for the lowermost stratosphere, Logan et al. (2012) found no trends in ozone for the decades 1978–1989, 1990–1999, 2000–2009, except for a marginally significant decrease in winter for 1978–1989, driven by very low values in early 1989 and an increase in winter and spring for 1990–1999. They found no evidence in the time series for the lowermost stratosphere from either ozonesondes over North America (Tarasick et al., 2005) or from satellite data (McPeters et al., 2007) to suggest that changes in stratospheric input can explain the increase in ozone over Europe in the 1980s. However, increases in stratospheric ozone after 1993 may have contributed to the increase in tropospheric ozone in the 1990s.

2.2 Changing ozone – a brief history

The German chemist C.F. Schönbein is credited with the discovery of ozone in 1839 (Schönbein, 1843) and its presence in the atmosphere was one of his earliest concerns (Braslavsky and Rubin, 2011). Early work by Hartley identified its UV spectrum and its role as a UV filter in the atmosphere (Hartley, 1881).

Modelling studies coupled to limited surface measurements from the late 1800s and early 1900s indicate that ozone concentrations have changed across all scales of the troposphere during the modern era due to enhanced emissions of precursors from industrialisation. A recent assessment (Cooper et al., 2014) of the most reliable historical ozone records (reliable due to the quantitative measurement methods employed), indicates that tropospheric ozone levels in western Europe increased by a factor of

3–5 between the late 1800s and late 1900s, and by a factor of 2 between the 1950s and 1990s (Wilson et al., 2012; Parrish et al., 2012; Marenco et al., 1994; Staehelin et al., 1994; Volz and Kley, 1988). Many locations around the world monitored ozone in the late 1800s and early 1900s using the semi-quantitative Schönbein ozonoscope (Marenco et al., 1994; Bojkov, 1986). These estimates indicate that ozone was much lower in those days compared to modern times, but the uncertainty of the measurements is so great that no accurate estimate can be made of the absolute increase in ozone (see the review by Cooper et al., 2014).

Recent modelling studies (Young et al., 2013; Lamarque et al., 2005) suggest that the tropospheric ozone burden in 1850 was 30 % lower than the present day (see Fig. 5), with the largest contribution to the change coming from the Northern Hemisphere extratropics. Most current global models are still unable to reproduce the low surface ozone concentrations reliably observed at Montsouris near Paris at the end of the 19th century (Young et al., 2013; Hauglustaine and Brasseur, 2001), despite the models having more detailed chemistry schemes, improved emissions estimates and finer spatial resolution (e.g. Lamarque et al., 2010). This suggests either problems with interpretation of the original observations and their context, or weaknesses in our assessment of precursor emissions or in our current understanding of atmospheric processes (Mickley et al., 2001). However, the inclusion of bromine chemistry can help models to approach the low ozone values measured at Montsouris in the late 1800s (Parrella et al., 2012).

Establishing quantitative ozone trends from observations is important for testing our understanding of the processes affecting ozone in the troposphere and for the attribution of these ozone changes to changes in precursor emissions, removal processes and meteorology. It is also important from an air quality perspective for determining the effect of emission controls and for identifying the extent to which surface ozone is locally or regionally controllable. Observed ozone trends are a challenge to interpret as there are a number of factors that may be responsible (Cape, 2008) including (a) changes in anthropogenic emissions of precursors (local, regional and global), (b) effects of biomass burning (both regional and global), (c) changes in Stratosphere–Troposphere exchange, (d) changes in geographical emission patterns and (e) changes in meteorological transport patterns. Long time series of high quality measurement data are required in order to detect the trend above the large inter-annual variation (Staehelin, 2003; Weatherhead et al., 1998, 2002) and the sensitivity of the extracted trends to location necessitates that this is done at a range of sites to ensure representativeness and permit attribution of the observed changes. Jonson et al. (2006) have discussed some of these effects in relation to ozone trends.

Global tropospheric ozone trends were recently assessed by the Intergovernmental Panel on Climate Change (IPCC, 2013), and by Cooper et al. (2014) who provided an expanded discussion and update to the IPCC assessment. Following is a summary of the findings from Cooper et al. (2014). Prior to the 1970s, the only rural or remote quantitative ozone measurements outside of western Europe were some short-term observations from Antarctica (Wexler et al., 1960) and Mauna Loa, Hawaii (Junge, 1962) during the late 1950s. By the early and mid-1970s quantitative and continuous ozone measurements were made at several rural and remote locations around the world for the purposes of detecting long-term changes in the global composition of the atmosphere. Continuous records in southern Germany began at the rural hilltop site of Hohenpeissenberg in 1971 and the mountaintop site of Zugspitze (2670 m) in 1978, and measurements began at the summit of Whiteface Mountain in upstate New York in 1973. Ozone measurements at remote sites were established by the US National Oceanic and Atmospheric Administration at its baseline observatories of Mauna Loa, Hawaii (1973), Barrow, Alaska (1973), the South Pole (1975), and American Samoa (1976) (Oltmans et al., 2013). Routine ozonesonde profiles became available in Germany, the US, Japan and Antarctica in the early 1970s (Oltmans et al., 2013) and ship-borne monitoring of the marine boundary layer of the North and South Atlantic Oceans began in the late 1970s (Lelieveld et al., 2004). The number of urban rural and remote monitoring sites has continued to grow from the 1970s to the present day.

All available Northern Hemisphere surface monitoring sites indicate increasing ozone from 1950–1979 until 2000–2010, with 11 of 13 sites having statistically significant trends of 1–5 ppbv decade^{-1}, corresponding to > 100 % ozone increases since the 1950s, and 9–55 % ozone increases since the 1970s. In the Southern Hemisphere only 6 sites are available since the 1970s, all indicating increasing ozone with 3 having statistically significant trends of 2 ppbv decade^{-1}. Ozone monitoring in the free troposphere since the 1970s is even more limited than at the surface. Significant positive trends since 1971 have been observed using ozonesondes above Western Europe, Japan and coastal Antarctica (rates of increase range from 1–3 ppbv decade^{-1}), but not at all levels. In addition, aircraft have measured significant upper tropospheric trends in one or more seasons above the north-eastern USA, the North Atlantic Ocean, Europe, the Middle East, northern India, southern China and Japan. Notably, no site or region has shown a significant negative ozone trend in the free troposphere since the 1970s. From 1990 until 2010, surface ozone trends have varied by region. Western Europe showed increasing ozone in the 1990s followed by a levelling off, or decrease since 2000. In the eastern US rural surface ozone has decreased strongly in summer, is largely unchanged in spring, and has increased in winter. In contrast, few rural sites in the western US indicate decreasing ozone, with half of all rural sites showing a significant increase in spring. The decrease in ozone in Europe and the eastern USA is consistent with the decrease in ozone precursors in those regions. Meanwhile in East Asia surface ozone is generally increasing where ozone precursor emissions are growing.

Parrish et al. (2013) demonstrate that another manifestation of changes in tropospheric O_3 is a shift of the seasonal cycle at northern mid-latitudes so that the observed peak concentrations now appear earlier in the year than they did in previous decades (see Fig. 6). The rate of this shift has been about 3 to 6 days per decade since the 1970s. Parrish et al. (2013) put forward an untested hypothesis that this shift may be due to changes in atmospheric transport patterns combined with spatial and temporal changes in emissions. This study relied on three long term (> 20 years) rural datasets in western Europe and one in the western USA. Cooper et al. (2014) also explored this topic using 21 year data sets from one additional site in western Europe and 5 additional sites in the USA, all in rural locations but more heavily influenced by regional ozone precursor emissions than those examined by Parrish et al. (2013). Of these 6 sites only three showed an earlier seasonal ozone peak, therefore the seasonal shift in the ozone cycle is not universal for time periods of 21 years or less.

Episodic peak ozone levels in rural areas of Europe have been declining during the last three decades due to regional pollution emission controls applied to the VOC and NO_x emissions from fossil fuel combustion associated with motor vehicles and power plants (Jonson et al., 2006; Jenkin, 2008; Derwent et al., 2010). Long-term downward trends have been observed at many long-running rural monitoring stations in the EMEP ozone monitoring network, and appear to be more pronounced at those stations where initial episodic peak levels were highest and insignificant at those stations where initial levels were lowest (Derwent and Hjellbrekke, 2013). The decreasing trend of highest percentiles is compatible with the known emissions reductions since 1990 (Vautard et al., 2006), and this behaviour has also been interpreted as resulting from the combined effect of regional pollution controls and increasing hemispheric ozone levels (Derwent and Hjellbrekke, 2013). In contrast, episodic ozone levels in the high NO_x environments of major European towns and cities are now rising towards the levels found in the rural areas surrounding them, as exhaust gas catalysts fitted to petrol and diesel motor vehicles reduce the scavenging of ozone by chemical reaction with emitted nitric oxide.

Whereas the vast majority of the scientific literature on ozone trends relies on rural supersites dedicated to the assessment of long term atmospheric change, the records of regulatory monitoring networks are becoming progressively long enough to complete such assessments. In the 1990s European air quality legislation began to include some targets with regards to the ozone monitoring network, so that the network now includes several thousand sites, a few hundred of which have records longer than 10 years. The size and diversity of the data gathered in the Airbase repository (maintained by EEA) offers an unprecedented view into air quality trends in Europe, provided that (1) 10 yr records can be considered long-enough to assess trends, and (2) the station representativeness of thousands of urban and rural background sites can be compared to the handful of supersites used elsewhere. Colette et al. (2011) and Wilson et al. (2012) propose such assessments and conclude that the dominating picture is towards an increase of ozone in urban areas or non-significance of the trends. They both report that the fraction of sites with an increasing trend is smaller when looking at peaks compared to daily means, but their findings suggest that the earlier reports of opposite signs of trends (Vautard et al., 2006) does not hold for this more recent period using this alternate monitoring dataset. By including urban stations in their analysis, Colette et al. (2011) also find an enhanced contribution of upwards trends, hence consolidating the results of Derwent and Hjellbrekke (2013) regarding the fact that urban areas are gradually becoming closer to rural levels.

The anthropogenic contributions to the observed trends are difficult to extract from the measurements, and reflect changes in both the magnitude and distribution of precursor emissions. While global average ozone responds to changes in global precursor emissions, trends at a given location are influenced by local, regional and global emission changes that may offset each other. Multi-model ensemble studies of the contribution of regional anthropogenic emission changes to regional and global surface ozone conducted under the LRTAP task force on Hemispheric Transport of Air Pollution, HTAP, (Fiore et al., 2009; HTAP, 2010) have been used to assess the relative contributions of long range transport and regional emission changes to regional ozone (Wild et al., 2012). These show annual mean surface ozone increases of nearly 0.3 ppb yr^{-1} at northern mid-latitudes between 1960–1980, similar to observed changes (e.g., Parrish et al., 2012), but small net decreases in surface ozone over Europe and North America since 1990 when anthropogenic emissions over these regions are believed to have peaked. A recent comparison between ozone observations at northern mid-latitudes and output from three current chemistry-climate models shows that the models (1) overestimate ozone mixing ratios, on average by ~ 5 to 17 ppbv in the year 2000, (2) capture only ∼ 50 % of ozone changes observed over the past five to six decades, and little of observed seasonal differences, and (3) capture ∼ 25 to 45 % of the rate of change of the long-term changes (Parrish et al., 2014). These differences may reflect poor representation of emission changes or ozone changes due to natural sources, or they may reflect more fundamental weaknesses in resolving key chemical or dynamical processes over continental regions. Further detailed analysis of the spatial and seasonal variability of local and regional ozone trends should provide a more critical test of our current understanding of the processes affecting ozone as represented in current models.

2.3 Ozone precursors

The spatial and temporal distribution of ozone and its precursors are in large part driven by the distribution of their emissions. An accurate knowledge of the surface emissions and of their evolution with time is therefore essential to support the analysis and modelling of air quality and climate change interactions. Up-to-date and consistent emissions are moreover required for the forecasting of the atmospheric composition (Frost et al., 2012).

Gridded global, regional, and national emission estimates exist for many of the pollutants that are important for understanding and analysing the distribution of ozone and its precursors, i.e. NO_x, CO, CH_4 and volatile organic compounds (VOCs). Some of these inventories are publicly available, whereas others are developed by individual research groups or government agencies to study specific aspects of emissions or atmospheric processes and are not always easy to access. In this paper, we will focus only on publicly available datasets.

Some inventories provide global coverage with relatively coarse spatial resolution, while others focus only on a specific region for selected species, and provide information at a very high spatial resolution; other inventories consider only specific sectors (such as traffic, shipping, etc.)

Over the past few years, several inventories providing the distribution of surface emissions of gaseous and particulate species were developed, at both the global and regional scales. This section will review the main advances during the past few years concerning surface emissions having the potential to impact ozone distributions and trends. The section will also discuss the current information on emissions uncertainties and will briefly review the most recent studies using inverse modelling techniques to evaluate and optimize emission inventories.

2.3.1 Quantification of global emissions of ozone precursors during the past decades

Most anthropogenic emissions estimates are developed using the same methodology, based on the product of estimates for activity data for different sectors and emission factors (mass emitted per activity unit). Activity data are obtained from records provided by different countries or from international organizations such as the International Energy Agency or the United Nations. This leads to a country-based quantification of emissions, which are then gridded using different types of proxies such as population, traffic, ship routes or location of power plants/factories. The quality of the gridding depends on the quality and availability of the proxies, and therefore varies strongly among the different regions of the world.

The data used for the quantification of emissions are not always consistent and many inventory developers adjust these data based on expert judgment. A priori emission factors are not always available or reported for all countries and for the differing emission sectors. They depend on different factors such as the level of economic development and the type of technology used in each region.

The emissions inventories developed in the past years cover both global and regional scales. Some of these inventories provide emissions at the country level; some provide emissions for a few species or for a larger number of species, and some provide emissions for one year, a few years or a few decades. The main inventories providing emissions of gaseous and particulate compounds currently used in global modelling or analysis of the atmospheric composition at the global scale and its evolution are: ACCMIP (1850–2000 on a decadal time scale; Lamarque et al., 2010) and its extension MACCity (monthly averages for the 1980–2010 period; Granier et al., 2011); EDGARv4.2 (1970–2008; Janssens-Maenhout et al., 2011) and HTAPv2 (2008 and 2010; Janssens-Maenhout et al., 2012); ECLIPSE (2005–2050; Klimont et al., 2013a); RETRO (1960–2000; Schultz et al., 2007a); HYDE (1890–1990; van Aardenne et al., 2001); POET (1990 and 2000; Granier et al., 2005); EDGAR3.2 (year 2000; Olivier et al., 2005).

Several inventories also provide emissions at the regional scale for different regions of the world. Among these inventories, the TNO-MACC (Kuenen et al., 2011) and TNO-MACCII (Kuenen et al., 2014) provide emissions for Europe at a high spatial resolution (1/8th x 1/6th degree), based on the EMEP (Droge et al., 2010) emissions reported by the European countries. In North America, the US Environmental Protection Agency (EPA) provides emissions since 1980 for the USA (available at http://www.epa.gov/ttnchie1/), and Environment Canada provides non-gridded emissions for Canada since 1985 (available at: http://www.ec.gc.ca). Inventories are provided for Asia by the REAS-v1 ($0.5^{\circ} \times 0.5^{\circ}$ spatial resolution; Ohara et al., 2007) and REAS-v2 ($0.25^{\circ} \times 0.25^{\circ}$ spatial resolution; Kurokawa et al., 2013a). The MEIC dataset (available at meicmodel.org) also provides emissions for China, at a $0.25^{\circ} \times 0.25^{\circ}$ resolution, and Sahu et al. (2012) provide emissions at a $1^{\circ} \times 1^{\circ}$ resolution for India, as well as Garg et al. (2006, not gridded emissions). Recently, an inventory was also developed for Africa by Liousse et al. (2014) at a $0.25^{\circ} \times 0.25^{\circ}$ spatial resolution.

2.3.2 Evolution of emissions in different regions since the 1980s

During the past three decades and the past few years, surface anthropogenic emissions have shown large changes in a few regions of the world. This section will focus on changes in emissions in Europe, North America and Asia. There is still little information on emissions changes in other areas of the world, and no detailed evaluation of the trends in emissions in these other regions can be made.

a. Emissions in Europe and North America

The implementation of emissions policies reductions in Europe and in North America over the past few decades has led to significant decreases in the emissions of ozone precursors. The agreement between available global and regional inventories is rather good among the global and regional inventories providing emissions of CO and NO_x for Europe and of NO_x for North America, with differences of 20–30 % between the lowest and largest proposed values. However, larger differences are obtained between inventories providing CO in the USA and NMVOCs in all regions, as shown in Fig. 7.

A detailed analysis of the changes in emissions of ozone precursors in Europe between 2003 and 2009 has been performed by Kuenen et al. (2014). This analysis has been extended in Fig. 8 by adding emissions for USA and in Canada for the same period. These data highlight the significant decrease in the emissions of NO_x, CO and NMVOC over the European and North American continental regions. The changes in Fig. 8 include shipping activities around Europe and the European seas. In contrast to industrial activities and to transportation in continental areas of Europe and North America, policies leading to the reduction of emissions from shipping have not yet been defined or implemented, resulting in significant increases in these emissions.

It is worth noting that nearly 70 % of ship emissions occur within 400 km of coastlines, causing air quality problems through the formation of ground-level ozone, sulphur emissions and particulate matter in coastal areas and harbours with heavy traffic (Eyring et al., 2010). Offshore shipping sources of NO_x may become significant as land based-emissions decline (Eyring et al., 2010; Jonson et al., 2009; Dalsøren et al., 2010). The impact of ship emissions on tropospheric oxidants is mainly caused by the relatively large fraction of NO_x in ship exhaust. Dalsoren et al. (2010) have shown that typical increases in yearly average surface ozone concentrations in the most impacted areas from shipping emissions are 0.5–2.5 ppbV. Transport emissions are predicted to be a significant contributor to US and European ozone by 2050 (Hauglustaine and Koffi, 2012).

b. Emissions in Asia

Emissions in Asia have shown dramatic increases over the past few years, which are now well documented, more particularly for China. Figure 9 shows the changes in the emissions of NO_x, CO and SO_2 for different Asian regions since 1980: the data in Fig. 9 highlight the very large increase in NO_x emissions in China over the past few years. The main reason for these emissions changes are increases in coal use for energy generation and industrial activities, as well as a large increase in the number of vehicles (Kurokawa et al., 2013b). Zhao et al. (2013) have examined the impact of anthropogenic emissions control in China and have shown that these control measures have led to a decrease in the emissions factors and emissions for most compounds, except for nitrogen oxides.

Comparisons between the regional and global inventories show significant differences, as shown in Fig. 10 (Granier et al., 2014): these figures show the total anthropogenic emissions of NO_x in China and India from 1980 to 2010, based on the data provided by the inventories mentioned in Sect. 2.3.1. All the inventories show an increase in the emissions over the years of the NO_x emissions, but the magnitude of the emissions and the rate of increase differ significantly between the datasets. There is a difference of about 50 % between the lowest and highest total emissions in China. For India, the values proposed by the different groups are even larger, with a factor of about 2.5 between the lowest and highest emissions. Since NO_x concentration levels are a key factor in the production of ozone (see Sect. 2.1), such large differences in the emissions could make the analysis of ozone concentrations and their trends rather difficult to achieve.

It should be noted that Fig. 10 does not display any evaluation of the uncertainties on the inventories: since the data used for developing the inventories (activity

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data, emission factors) are not provided with estimates of the uncertainties, no estimation of the uncertainties on the emissions can be made.

2.3.3 Uncertainties in anthropogenic emissions in different regions

As indicated in the previous section, most emission datasets are provided without any information on uncertainties on the data used for quantifying the emissions. Several sources of uncertainties have been identified, which will be summarized in this section.

Activity data and emission factors are generally provided without any information on their uncertainties. Emission factors are empirical functional relations between pollutant emissions and the activity that causes them: a comparison of emission factors is shown on Fig. 11, which displays measurements of emission factors in Chinese cities from different studies (Huo et al., 2012). This study has shown that the differences between emission factors are larger for older vehicles than for newer vehicles, which could be an indication of deterioration of emissions when vehicles get older.

The seasonal, weekly and daily variations of the emissions are generally not provided with inventories, and are not well characterized. Simple temporal profiles have been developed to describe the changes in emissions over a day, a week and a season, as shown in Fig. 12 for the European LOTOS-EUROS model (Kuenen et al., 2011). These profiles depend on the emission sectors. The same diurnal profiles are applied for all days of the week and to every country in the model domain for all periods, without taking into account differences in the way of living in different countries and its change with time. Similar profiles are not available for most the countries of the world, leading to large uncertainties in the temporal profiles of the emissions.

Good speciation of the NMVOCs lumped species is important for inventories. The translation of speciation into global and sometimes regional models chemical schemes is generally poor: a gridded speciated dataset has been developed as part of the RETRO inventory (Schultz et al., 2007a), and has not been revised or updated since. This speciation is currently applied to most global inventories, for all the past and future decades. In different regions, VOC speciated inventories have been developed for

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specific emission sectors often based on few individual measurements that are extrapolated with dubious reliability to related unmeasured emission sources. An example of such a speciation is shown in Fig. 13 for China (Wei et al., 2008). Li et al. (2014) have developed a speciation for Asia, which provides emissions of a large set of VOCs for different model chemical schemes, for individual VOCs and lumped species.

Detailed information of the proxies used for the determination of the distribution in space of the emissions, i.e. on the proxies used for gridding emissions are also lacking. Other large uncertainties on the emissions are linked with resources (oil and gas) extraction and flaring, and to inland and international shipping. Emissions from agricultural practices (cattle, fertilizers, agriculture waste burning) are also very uncertain.

In order to summarize the uncertainties on anthropogenic emissions, we have calculated, for all the inventories mentioned in Sect. 2.3.1 the minimum, average and maximum values of the emissions for different world regions for NO_x, CO and NMVOCs emissions in 2005. The ranges shown in Fig. 14 cannot be considered as a quantification of uncertainties, but they provide information on the differences between currently available datasets. Detailed evaluations of the uncertainties on anthropogenic emissions have started: for example, a methodology applying Monte Carlo simulations to quantify the uncertainties, represented as probability distributions, for the emissions of several compounds in China was proposed by Zhao et al. (2011).

Figure 14 also highlights the growing of emissions in Africa and the rest of Asia (all Asian regions except China and India), regions where more detailed information is required for a better analysis and modelling of the global atmospheric composition.

2.3.4 Emissions from fires

In the last few decades biomass burning has been recognized as an important source of ozone precursors (Hao and Liu, 1994; Schultz et al., 2008). Since wildfires are strongly dependent on meteorological conditions, drought episodes and human behaviour, they have a large interannual variability (Duncan et al., 2003), and the resulting emissions are very variable in time and space. It is therefore important to accurately characterize fire emissions, since they will partly drive the short-term variability of ozone precursors and ozone (Parrington et al., 2012). A review of the impact of biomass burning emissions on ozone was published by Jaffe and Wigder (Jaffe and Wigder, 2012).

The first inventories relied on data reported by forest services, observations from the ground and from aircraft. Since the late 1990s, several inventories providing emissions from fires have been developed based on observation of active fires and burnt areas by satellites, and more recently of fire radiative energy. Other inventories have also been developed, through the representation of fires in biogeochemical models. The most recent global datasets providing a spatial distribution of the emissions of ozone precursors from fires are: MACCity (monthly, 1960–2008, 0.5° × 0.5° resolution; Granier et al., 2011), GFAS (daily, 2003 to present, 0.5° × 0.5° resolution; Kaiser et al., 2012), GFEDv2 (monthly, 1997–2010, 0.5° × 0.5° resolution) and GFEDv3 (monthly, 1997–2010, 0.5° × 0.5° resolution) (van der Werf et al., 2006, 2010), IS4FIRES (daily, 2000–2013, 0.1° × 0.1° resolution, Sofiev et al., 2009), FINN (daily, 2002-current, 1 × 1 km resolution, Wiedinmyer et al., 2011), GUESS-ES (monthly, 1970–2009, 1° × 1° resolution, Knorr et al., 2012), GICC (monthly, 1900–2005, 0.5° × 0.5° resolution, Mieville et al., 2010), Kloster (monthly, 1900–2004, 1.9° × 2.5° resolution, Kloster et al., 2010), RETRO (monthly, 1980–2000; 0.5° × 0.5° resolution, Schultz et al., 2008).

The inventories providing daily emissions have highlighted the very large variability of emissions from fires in the different regions of the world. Only datasets providing emissions at a high temporal resolution are able to provide information on short and intense fire episodes, which happen often in different regions of the world, as a result of specific weather conditions or human-ignited fires. An example of this variability is shown on Fig. 15, from the FINN datasets (Wiedinmyer et al., 2011), which highlights the constant high fire episodes in each hemisphere.

Several studies have evaluated the differences between estimates of fire inventories, and have highlighted the large differences remaining between available datasets in different regions. Figure 16 displays a comparison of several of the datasets previously detailed, for carbon monoxide in Africa and South America (from Granier et al., 2011). Differences in the emissions for each year, as well as in the interannual variability of the emissions are very large. It should be noted that the AMMA inventory for Africa, which includes the use of satellite observations as well as local information on the fires provides significantly larger emissions than the other inventories, which are based either on satellite data only, or on fire modelling.

Another view of the differences between datasets is provided in Fig. 17, where CO emissions from different estimates are reported for different biomes (from Kaiser et al., 2013). The largest differences are reports for peat and savannah fires. The seasonal variation shown in these datasets is relatively consistent, except for temperate forests, where the consistency is very low.

The differences shown in Fig. 17 demonstrate a limit to the accuracy of emissions resulting from biomass burning. In turn, these impact on the distribution of ozone precursors and ozone through uncertainties on burned area, fuel load, emission factors and injection heights.

Data on burned areas from long-term monitoring have become available only recently, i.e. after 1995, and these data have been evaluated only for a few regions. The satellite data provide good information on spatial and temporal patterns of fire occurrence, but so far they have not provided quantitative information with high accuracy (e.g., Giglio and Kendall, 2004). These data complement data on fires in the mid-latitude regions, which are well monitored in many countries. However, monitoring by tropical countries is still scattered and scarce, owing to limited resources at the local level for records and accessibility. The effect of temporal resolution of fire emissions on models has been recently explored (Marlier et al., 2014).

The amount of fuel load and the combustion factors are calculated either from ecosystem models or through empirical formulas: these quantities depend on the fire severity, the fuel characteristics (foliage and biomass density, moisture, vegetation type, organic content and moisture of the soil) and the rate of spreading. These factors are highly variable and different studies have shown that large uncertainties still remain on the spatial and temporal variation of this quantity. A study by Knorr et al. (2012) has shown that the choice of the burned area dataset has by far the largest impact on interannual variability of simulated emissions, and that for the quantification of the total global emissions, burned area and combustion completeness have the largest impact on emissions for most species.

Emissions factors for the different species are generally taken constant for each type of ecosystem in different countries. However, emissions from a fire depend on the fuel type and fire characteristics, and they are often poorly determined. Most inventories currently use the emission factors compiled by Akagi et al. (2011) or the Andreae and Merlet (2001) compilation and following updates. Results from different studies nevertheless stress that more complete combustion, as in flaming fires, would lead to a larger fraction of highly oxidized species (e.g., CO_2, NO_x), while smouldering fires release more material in reduced form (e.g., CO, NH_3 and NMVOC species), which indicates that emission factors may vary with season, and that fire characteristics can be very different from one fire to another even within the same geographical location. Emissions factors from peat fires are not well quantified with different studies reporting a wide range of values (Akagi et al., 2011).

The lifetime of the species released in fires depends on chemical processes in fires plumes and therefore on the vertical distribution of the plumes. The plume injection height can be critical in the impact of biomass burning. Several studies have proposed plume models or parameterization of the top height of the plumes, based on empirical methods or on the use of satellite observations (Tosca et al., 2011; Martin et al., 2010). A determination of the vertical profiles of fires emissions at the global scale was proposed by Sofiev et al. (2013), based on satellite observations and semi-empirical formulas. An example is shown in Fig. 18, which highlights the importance of meteorology in the day-night variation of the height of fire plumes. The influence on ozone can be a combination of injection height and frequency (Williams et al., 2012).

2.3.5 Natural emissions

Natural processes in the atmosphere, vegetation and oceans lead to the emissions of a wide range of compounds (Granier et al., 2004). Emissions resulting from lightning are discussed in Sect. 4.7. This section only focuses on emissions of hydrocarbons from vegetation, since they can have a large impact on the distribution of ozone and its precursors and because terrestrial vegetation is the dominant source of atmospheric VOCs (Guenther et al., 1995). The emissions of isoprene and monoterpenes are the largest, but many other compounds are also emitted. Many studies performed during the past few years have used MEGAN (Model of Emissions of Gases and Aerosols from Nature) to quantify the emissions of biogenic VOCs to the atmosphere. MEGAN is a model system calculating temporal and spatial rates of emission of chemical compounds from terrestrial ecosystems to the atmosphere under varying environmental conditions. It was first introduced by Guenther et al. (1993, 1995, 2006, 2003). The most recent version of the model, MEGAN v2.1 was introduced in Guenther et al. (2012) and Sindelarova et al. (2014). The current algorithm takes into account the impact of past and present temperature, light (sun-lit and sun-shaded leaves), leaf age, and losses of primary emissions in the canopy and soil moisture.

Examples of emissions of isoprene, monoterpenes and methanol in 2003 are shown in Fig. 19, together with the relative contribution of the different biogenic VOCs to the total amount emitted. Isoprene emissions account for 56 % of the total, which indicates that the emissions of the other BVOCs and their chemical oxidation schemes (see Sects. 4.3 and 4.10) also need to be taken into account when simulating atmospheric composition.

Previous studies show significant differences between the total amount of BVOCs emitted by vegetation (Sindelarova et al., 2014). These differences are related to the large uncertainties of different factors driving BVOCs emissions, such as radiation amount, leaf temperature, and parameterization of the soil moisture factor or the representation of canopy processes. There are also large differences in the vegetation types and in the distribution of plant functional types used in different models and/or their assignment with BVOCs emission activity.

Other methods have been used to calculate the emissions of BVOCs by the vegetation. Arneth et al. (2007) have for example calculated the emissions using a dynamic global vegetation model (LPJ-GUESS, Sitch et al., 2003) and a physiological BVOCs emission algorithm. Studies conducted using the LPJ-GUESS model (Arneth et al., 2011) have shown that variations of driving input data such as meteorology and vegetation description among different models might lead to substantially different emission estimates.

Figure 20 shows the differences between previous estimates of global total isoprene emissions: the difference between the lowest and largest estimate is 65 %. In Fig. 20, the three values indicated by green bars correspond to an optimization of isoprene emissions using inverse modeling techniques and formaldehyde satellite observations (see next section). The difference between the highest and lowest value is about a factor of two, which highlights the large uncertainties in the determination of isoprene emissions.

2.3.6 Evaluation and optimization of emissions using inverse modelling techniques

Inverse modelling techniques have been widely used during the past few years to optimize surface emissions so that simulated atmospheric concentrations can reproduce observed concentrations. Most recent studies either minimize the weighted distance between model and observations (variational approach) or minimize the error variance of the estimated parameters (Kalman Filter techniques) (Saide et al., 2011). Differences between the distributions provided by the models and the observations are not only due to inaccuracies on the quantification of emissions, errors in the model data (meteorological fields for example), but also in the representation of physical and chemical processes in the models: all these factors need to be taken into account in inverse systems (Elbern et al., 2007). Estimates of emissions using inverse techniques also depend on the a priori emission dataset used, on the meteorological fields used to drive the models used that infer emissions (Arellano and Hess, 2006), and on the data used in the optimization of the emissions (Hooghiemstra et al., 2012). A review of the current capabilities of inverse techniques to better quantify surface emissions in North America using satellite observations was published by Streets et al. (2013).

These techniques have been mostly applied to the species for which observations from satellite are available or for the optimization of local/regional emissions when comprehensive observation datasets exist. Therefore, most studies have discussed the optimization of greenhouse gases (CO_2 and CH_4), of ozone precursors CO and NO_2, of aerosols and their precursors (see Fuzzi et al., 2014, companion paper), and of biogenic emissions using satellite observations of formaldehyde.

Several studies have applied inverse modelling techniques to the optimization of CO emissions using observations from surface networks (Petron et al., 2004) as well as observations from the MOPITT and IASI satellite instruments. Most of these studies using satellite data have concluded that the a-priori anthropogenic emissions of CO might be underestimated as indicated in Fig. 21a (Fortems-Cheiney et al., 2011) and 22b (Tohjima et al., 2014), more particularly at mid-latitudes of the Northern Hemisphere in winter (Kopacz et al., 2010; Stein et al., 2014). However, an analysis of satellite and aircraft observations has also shown that emissions inventories in North America might provide overestimated values (Miller et al., 2008). Emissions resulting from fires have also been optimized, and showed that current surface inventories might underestimate fires in boreal regions (Pfister et al., 2005). Inverse techniques have also provided information on the seasonal cycles of emissions from fires, for example in Africa as shown by Chevallier et al. (2009).

Several studies have used satellite NO_2 column observations to constrain nitrogen oxide emission inventories through inverse or forward modeling (Martin et al., 2004; Kim et al., 2009; Lamsal et al., 2011; Wang et al., 2012). These studies exploited the relatively short lifetime of tropospheric nitrogen oxides, which ranges from several hours to a few days. As a result, NO_2 has its largest concentrations in the boundary layer close to emission sources, making measurements of NO_2 columns well suited to improving our knowledge of the emissions of NO_x. Two examples of optimizations of NO_x emissions using satellite observations are given in Fig. 22. Figure 22a shows a quantification of emissions trends in China as provided by an inventory optimized using the SCIAMACHY/GOME observations for the 1996–2004 period (Zhang et al., 2007). From 1996 to 2004, NO_x emissions over East Central China region increased by 61 % according to the inventory, while a 95 % increase in the NO_2 columns was obtained from the satellite observations during the same period. Stavrakou et al. (2008) have evaluated the changes in the emissions in different regions of the world from 1997 to 2006 using an inverse method and found larger increases in the optimized emissions when compared to prior emissions in the Far East region, and emissions decreasing faster than in the inventories in North America.

Optimization of the emissions of several other compounds have also been evaluated through inverse methods constrained by satellite observations, such as isoprene, methanol or formaldehyde (Stavrakou et al., 2011, 2009; Palmer et al., 2003; Wells et al., 2014; Barkley et al., 2013) and other studies have focused on the optimizations of the emissions from different sectors, such as ships (de Ruyter de Wildt et al., 2012; Vinken et al., 2014).

2.4 A climatological view of ozone/linkages across the scales

The available observations show that tropospheric ozone is highly variable both in space and time, on long and short scales. Over the remote oceans, observations show low ozone amounts within the tropical Hadley circulation with little or no vertical gradient in mole fraction, then higher concentrations at mid latitudes, with an increase with height, corresponding to the additional source of tropospheric ozone from STE as well as in-situ chemistry (see Figs. 23 and 24). Over the continents and nearby oceans in the lower troposphere different behaviour is observed depending on the level of the ozone precursors. Analysis of the seasonal-diurnal variations allows separation of the following types of ozone variations in the extra-tropics (Tarasova et al., 2007): clean background, rural, semi-polluted non-elevated, semi-polluted semi-elevated, elevated and polar/remote marine. For the “clean background” regime in the Northern Hemisphere the seasonal maximum is observed in March–April, both for night and day. For those sites with a double maximum or a wide spring-summer maximum, the spring maximum appears both for day and night, while the summer maximum is more pronounced for daytime and hence can be attributed to photochemical processes. There is much debate as to the origin of the spring maximum; it is likely a combination of dynamical/transport processes and photochemistry (Monks, 2000).

In July, northern summer, major regions of elevated lower troposphere ozone are observed over USA, Europe and East Asia from urban/industrial activities and regions of elevated ozone over the tropics due to both biomass burning and other human activities. Satellite observations of tropospheric ozone have revealed much detail about the spatial distribution including the discovery of the regional tropospheric ozone maximum off southwest Africa over the Atlantic Ocean (Fig. 23) and the oscillation of tropospheric ozone over the Indonesian Archipelago in synchronicity with El Niño (Ziemke et al., 2010). In highly dynamic regions such as the Mediterranean basin (Lelieveld et al., 2002, 2009), the strength of the meteorological systems (Azores anticyclone and Middle Eastern depression) are key factors in explaining both the variability and the anomalies of ozone in the lower troposphere in this region (Doche et al., 2014). Recent observations have suggested there is a summertime free tropospheric ozone pool over the Mediterranean (Zanis et al., 2014; Kalabokas et al., 2013).

The data in Fig. 23 clearly highlights the benefits offered by satellite data for investigating the global distribution of tropospheric ozone. However, it should be kept in mind that such data give an incomplete picture (Monks and Bierle, 2011) which requires complementary observing systems (Laj et al., 2009). For example, the AMMA campaign (Redelsperger et al., 2006) and associated analysis performed with the in-situ MOZAIC (Sauvage et al., 2005) and SHADOZ data (Thompson et al., 2003a, b) have revealed a somewhat different feature of ozone distribution (both in terms of amount of the tropospheric columns and in the location of the maxima) over Western and Southern Africa including the adjacent Atlantic Ocean. In July, when biomass burning mainly occurs over the southern tropical part of Africa, the tropospheric ozone column is about 45 DU over the continent (Thompson et al., 2014; Sauvage et al., 2005, 2006). Export of polluted air masses is observed throughout the Gulf of Guinea up to the coast of West Africa in the Northern Hemisphere. Reeves et al. (Reeves et al., 2010) provide a clear characterisation of the ozone distribution throughout the troposphere over West Africa during the monsoon period. Thanks to previous analysis based on MOZAIC data (Sauvage et al., 2007a, 2005) and the regular ozone soundings over Cotonou during 2 years (Thouret et al., 2009), it has been shown that the biomass burning seasons in both hemispheres impact the tropospheric ozone profiles in both hemisphere as well. As a consequence, a picture like the so-called "Ozone paradox" (Thompson and Hudson, 1999) was shown to be no longer valid (Sauvage et al., 2006) owing to the insight provided by additional in-situ observations. Recent work has shown evidence for the removal of ozone in Saharan dust plumes (Andrey et al., 2014) which is correlated with both dust loading and total amount of water present.

At coastal or island sites in the tropics diurnal variation in ozone generally show a minimum during the daytime. Occasional air transport events from the mid-latitudes bring in higher ozone concentrations (Lawrence and Lelieveld, 2010). The mole fractions are low, typically 5–20 ppb, and the annual maximum occurs in June to September, southern winter, a characteristic of ozone in the Southern Hemisphere troposphere. For more continental tropical regional sources of ozone due to precursor emissions from such activities as biomass burning (e.g. Ojha et al., 2014; Cristofanelli et al., 2010), land clearing, agriculture and human settlements may cause occasional elevated ozone concentrations. The seasonal ozone variation may be affected by these activities which can be influenced by seasonal meteorological conditions such as the occurrence of a wet/dry seasons (Valks et al., 2014; Rama Gopal et al., 2014; Cristofanelli et al., 2010). Under stable conditions, ozone depletion due to ozone deposition and NO titration will occur. The diurnal variation of ozone will generally be characterized by lower concentrations at night and higher concentrations during the daytime (see e.g.

Rama Gopal et al., 2014). Vegetation cover plays an important role together with local meteorology in (natural) trace gas emissions. For example, tropical forests and plantations are among the greatest emitters of isoprene, a reactive hydrocarbon species which is involved in the photochemical cycle of tropospheric ozone (see Sect. 4.3). Replacement of tropical forest by agriculture (e.g. palm trees) may cause potential future elevated ozone levels (Hewitt et al., 2009; MacKenzie et al., 2011) (see Fig. 25).

High latitude sites may be influenced by the near continuous presence of snow or ice cover (Helmig et al., 2007). Polar sites may have wind directions that remain relatively constant for months. Coastal sites may have ozone depletion events, which are related to halogen chemistry (Simpson et al., 2007), and which is evident for example at Barrow during northern spring, March to May (Oltmans et al., 2012). The high reflectivity of snow and ice influences the photochemical reaction rates, because more UV radiation is available than what would be expected for these latitudes if one assumes a global average value for the surface UV albedo. In stable conditions with bright sunlight, local photochemical production has been observed due to NO_x emission from the snow (Helmig et al., 2008a, b) and this is evident at the South Pole during November to February, centred on southern summer. The ozone concentrations in background air at the South Pole peak in winter/spring and fall to a minimum in summer/autumn as with other Southern Hemisphere sites.

Moving to the urban scale the local coupling of NO_x and O_3 is important in that reductions in NO can contribute to increases in ozone (Kley et al., 1994). In areas of high NO_x, as is often observed in urban areas, ozone levels can be suppressed through the following reaction:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R4}$$

This phenomenon, sometimes dubbed "NO_x titration", thereby leads to the counter-intuitive effect that reducing NO_x (NO) reduces the amount of ozone being suppressed and actually increases ozone (Heal et al., 2013; Sicard et al., 2013). The spatial variability of ozone in larger urban areas can be very much driven by "titration" (Escudero et al., 2014). Figure 26 shows the gradual increase in urban ozone, moving towards background levels, driven by reducing NO_x emissions over the last couple of decades in the UK, decreasing the suppression of ozone. Figure 27 shows the "titration" in urban areas across Europe from modelling studies, showing the widespread nature of this effect and the need to couple the regional and hemispheric picture to the urban. In a sense there is an urban decrement driven by this process. Conversely, there has been some work looking at megacity impacts on regional ozone (Tie et al., 2013; Beirle et al., 2011; Guttikunda et al., 2005) (see also Sect. 4.1).

Given the strong NO_x-O_3 (sometimes referred to as O_x, Zlatev et al., 1992; Yu et al., 2008, see also Fig. 27) couple at the urban scale there are a number of issues around the role of an increase in the NO_2:NO emission ratio caused by an increase in the share of diesel vehicles in Europe and the role that may play in ozone formation (Weiss et al., 2012; Carslaw et al., 2011; Carslaw, 2005). Further there are questions as to what extent spatially (along roadsides, across urban areas, regionally) primary NO_2 emissions affect ozone concentrations (see e.g. Yu et al., 2014). Meteorology also plays a large role in local scale ozone concentration affecting deposition and transport (e.g. Vieno et al., 2010; Francis et al., 2011) alongside transport and dispersion in urban landscapes such as street canyons etc. (see e.g. Baker et al., 2004; Zhong et al., 2014; Kwak and Baik, 2014). Urban areas are dynamic regions in terms of emmisions of ozone precursers that have seen strong changes owing to emmision reduction measures (see e.g. von Schneidemesser et al., 2010, 2011; McMeeking et al., 2012; Warneke et al., 2012; Vijayaraghavan et al., 2014).

3 Impacts

Surface level ozone has multiple impacts. As an oxidant it can induce respiratory problems and has been associated with premature human mortality (Bell et al., 2006; Gryparis et al., 2004). Further it can cause tree/vegetation damage (Krupa and Manning, 1988), reduce photosynthesis and growth (Reich and Amundson, 1985) and therefore crop yields (Fiscus et al., 2005) (see also Felzer et al., 2007; Ashmore, 2005 for recent reviews). Ozone is also an important greenhouse gas (IPCC, 2013).

3.1 Health

Ozone has long been known to cause adverse effects on health (Bates, 2005). The gas is a powerful oxidant and short-term inhalation induces inflammation of the entire respiratory tract, although the nasal cavity and the zone between the conducting and gas-exchange airways are potentially more susceptible. Significant inflammation can be detected at ambient levels of ozone in controlled human exposure studies, and although there is some degree of adaptation after repeated exposures, pulmonary inflammation may persist, mainly in the terminal bronchiolar units. As well as elucidating these effects in exposure studies, which naturally exclude the most sensitive or susceptible parts of the population, associations between ozone and mortality and morbidity have also been shown in epidemiological studies, covering the population at large.

Early work on ozone health effects involved mainly exposure studies in chambers. On the basis of this work ozone was included in the first tranche of National Air Quality Standards in the US, with a standard of 80 ppb as a 1 h average, promulgated in 1971 as part of the US Clean Air Act. In Europe, the first edition of the WHO “Air quality guidelines for Europe” in 1987 set a 1 h guideline value of 75–100 ppb. This guideline was also based primarily on chamber studies. Since then much more evidence has accumulated regarding ozone effects, not least from epidemiology studies, and in the 2005 Global Update (WHO, 2005) the most recent WHO Guideline is now 50 ppb expressed as the maximum 8 h mean in a day. The same document also sets an interim target of 80 ppb as a daily maximum 8 h mean, and a “High Level” of 120 ppb daily maximum 8 h mean where it notes that significant health effects could occur and that a “substantial proportion of vulnerable population affected” (sic).

Earlier WHO guidelines were based on these chamber studies on humans and animals, but the more recent 2005 Global Update from WHO mentioned above additionally used time series epidemiological studies (WHO, 2005). However, all guidelines up to and including 2005 referred to short-term exposures and health effects, but the 2005 report noted that at that time there was some evidence that long-term exposure to ozone may have chronic effects but the review concluded that the evidence was insufficient to recommend a guideline. The policy implications of these purely health-based guidelines are discussed in Sect. 5.

As part of their "Year of the Air" in 2013 the European Commission requested WHO to review the health effect evidence on the pollutants covered in EU air quality legislation, including ozone. The review was in two parts, firstly a review (REVIHAAP) of the health effect evidence itself, in the form of answers to policy-relevant questions prepared by the Commission, in consultation with the WHO. The final REVIHAP report is available at http://www.euro.who.int/__data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report-final-version.pdf. The second part of the process involved a shorter project (HRAPIE) which recommended concentration-response functions for use in health impact assessments and other quantification, for example in integrated assessment modelling to underpin the EU policy process. The HRAPIE report is available at http://www.euro.who.int/__data/assets/pdf_file/0006/238956/Health-risks-of-air-pollution-in-Europe-HRAPIE-project,-Recommendations-for-concentrationresponse-functions-for-costbenefit-analysis-of-particulate-matter,-ozone-and-nitrogen-dioxide.pdf.

The REVIHAAP report addressed three questions relating to ozone where WHO and the European Commission felt a more recent assessment was warranted. The questions posed were

1. What new evidence on health effects has emerged since the review work done for the 2005 global update of the WHO air quality guidelines, particularly with regard to the strength of the evidence of the health impacts associated with short-term and long-term exposure to ozone?
2. What new health evidence has been published in relation to the evidence or likeliness(sic) of a threshold below which impacts are not expected? and

3. Based on currently available health evidence, what ozone metrics, health outcomes and concentration-response functions can be used for health impact assessment.

The answer to the first question noted that the earlier 2005 global update found evidence only for short-term effects on mortality and morbidity. However an important advance is that several cohort studies have now emerged showing associations between long-term exposures and mortality. Of particular importance are the studies using the large American Cancer Society cohort. A study (Krewski et al., 2009) using single pollutant models found an association between summertime average ozone and all-cause mortality as well as cardiopulmonary mortality, although the high correlation between $PM_{2.5}$ and ozone in the summer months made it difficult to separate the effects of the two pollutants. A further study using the same cohort (Jerrett et al., 2009) found unstable risk estimates for ozone and all-cause, cardiopulmonary and cardiovascular mortality with only respiratory mortality being associated with ozone after adjustment for $PM_{2.5}$. For a more detailed discussion of these and other recent cohort studies (Smith et al., 2009; Zanobetti and Schwartz, 2011; Lipsett et al., 2011) than space here permits, the reader is referred to the REVIHAAP report.

In answering the second question regarding evidence for a threshold, the REVIHAAP report noted that epidemiological studies reporting an effect of long-term exposures to ozone on mortality do not, in general permit the firm identification of a threshold. However the report did draw some conclusions which are helpful to health impact studies.

Earlier chamber exposure studies referred to above have been supplemented by more recent studies showing effects at lower levels. Studies since the 2005 global update have shown that healthy exercising human subjects showed impaired lung function at concentrations of 60 ppb for 6.6 h, relative to clean air controls (Kim et al., 2011). The report noted that the subjects were healthy adults and thus not representative of the general population, or of real-world combinations of susceptibility and exposure. The REVIHAAP report discusses a number of other studies which report adverse effects at concentrations lower than those in the above study and the reader is referred to that report for a more detailed discussion. The REVIHAAP report concluded that the evidence from epidemiological studies for a threshold for short-term exposures is inconsistent with some large multi-city studies which reported little evidence for a threshold down to near background ozone concentrations, whereas other short-term studies suggest a threshold between 10 and 45 ppb daily maximum 1 h ozone. The report concluded that in summary the evidence for a threshold for short-term exposure is inconsistent but where a threshold is observed it is likely to lie below 45 ppb maximum 1 h ozone.

The third question, relating to quantification of the health impacts of ozone overlaps with the HRAPIE project, the second part of the WHO review for the European Commission. The REVIHAAP report concluded that a range of health outcomes could be used where baseline rates are known, including all-age, all-cause, cardiovascular and respiratory mortality, and for ages 65 and over respiratory and cardiovascular hospital admissions. The report concluded that the evidence supports the use of all-year coefficients for daily maximum 8 h average ozone concentrations. Bearing in mind the discussions on a threshold REVIHAAP recommended that cut-off points be used at 35 ppb for daily maximum 8 h ozone "for consistency with previous work using SOMO35..." (for definition of SOMO see e.g. AQEG, 2009). In an important further step, the report also recommended using a cut-off at 10 ppb, I.e. SOMO10.

This latter step is significant in that use of SOMO10 in assessing the effects of most future control strategies already in place or proposed in Europe (and probably elsewhere) are likely to lead to increases in health impacts from ozone exposures. The conclusions of the HRAPIE report essentially endorsed the findings of the REVIHAAP report, suggesting the use of SOMO10 and SOMO35, and an assessment of long-term exposure impacts as a sensitivity study.

Interestingly, the Impact Assessment for the EU Clean Air package published on 18 December 2013 (http://ec.europa.eu/environment/air/clean_air_policy.htm) only used SOMO35 to assess the health impact of proposed policies. This was justified on the grounds that below this level there are uncertainties in ozone modelling. However, it is convenient that using SOMO35 minimises the impact of increased ozone health impacts which are likely to result if SOMO10 is used. The policy process has yet to come to terms with the possibility that existing and planned control measures are likely to result in increased health impacts from ozone if a low threshold, or a long-term (annual or summer) average concentration is used in impact assessments. A recent modelling study (Heal et al., 2013) which looked at the burden of health impacts from ozone in 12 regions in the UK incorporated the uncertainty over thresholds using a population weighted daily maximum 8 h mean ozone metric with a cut-off at 35 ppb and also with no threshold. They also incorporated future temperature increases and changes in the tropospheric baseline of ozone, and showed that as expected the assumption of zero threshold gave much larger health impacts. Moreover they showed that under a no-threshold assumption health impacts (deaths brought forward and hospital admissions) in the "current legislation" scenario *increase* due both to the no-threshold assumption but also with the assumption of an increasing tropospheric ozone baseline. This interplay between the threshold assumption and the future trend in the tropospheric baseline has important implications for policy as discussed in Sect. 5 below.

Finally, an interesting new development bridging the gap between atmospheric chemistry and epidemiology is a time-series study of the associations between O_x (defined as $O_3 + NO_2$) and health outcomes (Williams et al., 2014). As well as having a sound basis in atmospheric chemistry given the rapid interchange between ozone and NO_2, this also has a toxicological rationale since it is probable that both ozone and NO_2 cause harmful effects via oxidative stress (although it is recognised that NO_2 could also act via other mechanisms). The study showed that the associations between O_x and mortality were stronger than for either of the two pollutants individually, but similar to the pollutants when used in a two-pollutant model. The preliminary conclusion is that in epidemiological studies of either ozone or NO_2, some form of interaction should be incorporated, either as Ox or in a two-pollutant model. Single pollutant models for ozone or NO_2 should not be used.

3.2 Ecosystems

Ozone is phytotoxic. The primary ecosystem impact of ozone is via the stomatal uptake of ozone followed by reaction with the internal plant tissues generating highly reactive oxidants that interfere with physiological processes (see also Sect. 2.1.2) (Fowler et al., 2009; Matyssek et al., 2008, 2010). Ozone may also react with leaf cuticles and other external plant surfaces as well as the volatile compounds emitted by vegetation.

Ozone has been recognised as a pollutant causing damage to vegetation since the 1960s and a research programme to quantify crop loss in North America was established during the 1970s (Karnosky et al., 2007; Adams et al., 1982). These studies showed that reductions in exposure to ozone of 40 % would reduce the annual costs of ozone damage by USD 3 billion (at 1980 prices). These early studies used metrics for ozone exposure which were simply the product of ozone mixing ratio and time above a threshold value (40 ppb) and had units of ppb hours. Global modelling results show that China, India and the United States are currently by far the most affected countries, bearing more than half of all global losses and threatened areas from ozone crop exposure (Teixeira et al., 2011). Crops such as rice have shown sensitivity to ozone. Research in Europe has improved the methods of assessment and estimates of crop loss (Emberson et al., 2009). In the US context, recent work by Ye and Unger has shown that O_3 damage decreases GPP (Gross Primary Productivity) by 4–8 % on average in the eastern US and leads to significant decreases of 11–17 % in east coast hot spots (Yue and Unger, 2014). Crops such as rice have shown sensitivity to ozone (Ainsworth, 2008). Work in China has looked at the ozone exposure for rice regions, finding that regions along the Yangtze and south China had the highest risks in 2000, and these risks will double or triple by 2020 (Tang et al., 2014). It has been recently estimated that the nationally aggregated yield loss owing to ozone in India is sufficient to feed about 94 million people living below the poverty line (Ghude et al., 2014). Future moves to biofuel crops could enhance the formation of ozone with concomitant negative health impacts (Ashworth et al., 2013; Hardacre et al., 2013).

Ozone risks for crops and pastures depend on exposure, leaf uptake and the plant's defence capacity (Fuhrer, 2009; Kangasjarvi et al., 1994). The extent of ozone damage has been shown to be directly proportional to the stomatal ozone flux for a range of crop plants in excess of a threshold value, recognising that vegetation has an innate capacity to detoxify oxidants (Fowler et al., 2009). Recent analyses have shown a crop loss of 14 % due to ozone in the year 2000, equivalent to 3.2 billion Euros (Mills et al., 2011). The same authors show that semi-natural vegetation has a similar range of sensitivity to ozone as crop plants and is a cause of decreased productivity of European forests. It has been argued that plant breeding that incorporates O_3 sensitivity into selection strategies will be increasingly necessary to achieve sustainable production with changing atmospheric composition (Booker et al., 2009).

The reduced carbon assimilation due to ozone by forests globally has been estimated by Sitch et al. (2007) to represent a substantial contribution to the indirect radiative forcing of climate by ozone (see Fig. 28). Through these effects on the productivity of ecosystems and the potential effects on biodiversity, ozone has become the most important pollutant threat to terrestrial ecosystems globally and is likely to remain so through most of the current century. Witting et al. (2009) have shown that the carbon-sink strength of Northern Hemisphere forests is likely reduced by current ozone and will be further reduced in future if ozone rises therefore implying that a key carbon sink currently offsetting a significant portion of global fossil fuel CO_2 emissions could be diminished or lost in the future (Wittig et al., 2009).

In a recent review Fuhrer looked at the ozone risk for crops and pastures in respect of future climate and concluded that the facets of exposure, leaf uptake and the plant's defence capacity are likely to change with a combination of changing anthropogenic ozone precursor emissions and climatic conditions. For example, in areas where the frequency of hot/dry periods is projected to increase ozone episodes may become more frequent and cumulative exposures will grow, but leaf uptake of ozone will decline. In contrast, in more remote rural areas with rapid warming and less drying, ozone risks are likely to grow because of increasing hemispheric transport of pollution leading to peak ozone levels at times when plant sensitivity is high (Fuhrer, 2009). Tai et al. (2014) have shown that warming reduces global crop production by $> 20\,\%$ by 2050. In the range of the scenarios used ozone changes either exacerbate or offset a substantial part of the climate impacts. The authors note that given the competing sensitivities to heat or ozone that it is possible to measure the relative benefits for climate adaptation vs. air pollution regulation for food security.

3.3 Impact of ozone on climate

Tropospheric ozone interacts with both solar (short-wave, SW) and terrestrial (long-wave, LW) radiation – consequently changes in its distribution can generate radiative forcings (RF) and lead to changes in climate. In their Fifth Assessment Report of climate change, IPCC found that changes in tropospheric ozone between 1750 and 2010 had generated a global mean radiative forcing of +0.40 (90 % confidence range: 0.20 to 0.60) $\mathrm{W\,m^{-2}}$ (Myhre et al., 2013).This was largely based on the ACCMIP assessment which considered changes in ozone (1850–2000) simulated by 17 different global models, and calculations from three different radiation schemes (Stevenson et al., 2013). The ACCMIP results were augmented by simulations back to 1750 and up to 2010 by the OsloCTM2 model (Skeie et al., 2011), and were broadly consistent with earlier assessments from the literature.

An important feature of the O_3 RF is that, in comparison to the RFs from the well-mixed greenhouse gases, it is more spatially variable (see Fig. 29). The largest changes in ozone since 1750 have occurred over the industrial regions that are the main sources of ozone's precursors (NO_x, CO, and VOCs) (see also Sect. 2.3). The industrial emission focus is tempered somewhat by ozone's other key precursor, CH_4, which is relatively well-mixed due to its decadal lifetime, and also by ozone's lifetime of a few weeks, which allows transport to reduce zonal heterogeneities. In addition, to the variations in ozone changes, the spatial distribution of the O_3 RF also depends on other factors. The LW RF is largest where the temperature difference between the surface and the tropopause reaches a maximum: that is over land in the tropics and sub-tropics. The SW RF is largest over more reflective surfaces e.g., snow/ice and desert. The presence of clouds reduces the LW RF, and also modulates the SW RF. This combination of contributing factors leads to the net (LW + SW) O_3 RF peaking over the southern margins of the northern mid-latitudes and sub-tropics over land, and in particular over N. Africa and the Middle East (Fig. 29).

Shindell et al. (2005, 2009) and Stevenson et al. (2013) have attributed the O_3 RF to O_3 precursor emissions (CH_4, NO_x, CO and VOCs). Results from these studies are reported in the "emissions-based" RF summary diagram of the IPCC-AR5-WGI Summary for Policymakers (IPCC, 2013). Stevenson et al. (2013) found that increases in anthropogenic emissions of CH_4, NO_x, CO and NMVOCs are respectively responsible for 44 ± 12 % (±1 SD range, based on results from 6 different global models), 31 ± 9 %, 15 ± 3 % and 9 ± 2 % of the 1850s–2000s ozone RF. All these O_3 precursors also affect the abundance of atmospheric OH, and hence the lifetime of longer-lived greenhouse gases such as CH_4. Consequently, emissions of ozone precursors generate further impacts on climate in addition to those related to changes in ozone; often these additional climate impacts occur over different timescales, and the net integrated impact on climate of emissions of a particular ozone precursor are complex to diagnose e.g. (Fuglestvedt et al., 2010). A further complication is that net impact on atmospheric composition, and hence climate, depends upon the location of ozone precursor emissions, both in the horizontal e.g., (Fry et al., 2012) and vertical e.g. (Stevenson and Derwent, 2009).

A major source of uncertainty in the O_3 RF is the pre-industrial distribution of ozone (see Sect. 2.2). The few measurements that do exist are mainly thought to be unreliable, but the two more rigorous datasets, from Montsouris in Paris and Pic du Midi, a mountain top site in central France (Marenco et al., 1994), suggest that current generation models significantly overestimate late 19th century ozone levels (Cooper et al., 2014). Cooper et al. (2014) highlight that global models significantly underestimate recent trends in surface ozone, suggesting that they overestimate past ozone levels. Consequently, there are suggestions that the ozone RF may be substantially underestimated (also see, e.g., Mickley et al., 2001). It is unclear how these apparent discrepancies in surface ozone translate into uncertainties in O_3 RF, which is more strongly related to changes in the upper troposphere. The error estimate quoted by IPCC makes only a cursory attempt to include this source of uncertainty. Other sources of uncertainty are estimated from the model spread in the 1850–2000 change in ozone, and differences between radiation schemes. Nevertheless, the uncertainties associated with O_3 RF are far smaller than those due to, e.g., aerosol, because the key source of uncertainty is the O_3 change rather than our understanding of the fundamental processes involved.

The spatial structure of the climate response to a particular radiative forcing is not directly related to the spatial distribution of the RF, but the climate response is typically spread out over the same latitudes e.g. (Shindell et al., 2010).

The efficacy, or relative effectiveness of an O_3 RF relative to a CO_2 RF in generating a global mean surface temperature change, has been estimated by Hansen et al. (2005) and Stuber et al. (2005). For stratospherically adjusted RFs, Stuber et al. (2005) found that the tropospheric O_3 efficacy has values in the range 0.7–1.7, with O_3 changes in the lower troposphere showing higher efficacies than the upper troposphere, and O_3 changes in the extra-tropical N. Hemisphere showing higher efficacies than globally uniform changes. The spatial dependence of the efficacy appears to relate to the interactions with climate feedback mechanisms e.g., Shindell (2014).

It is quite arbitrary (and often scientifically dubious) to consider RFs owing to ozone changes in the troposphere and stratosphere separately, not least because the tropopause is often difficult to locate (e.g., Prather et al., 2011), and because coherent ozone changes often straddle the tropopause e.g. (Gauss et al., 2006; Shindell et al., 2013). Changes in tropopause height and morphology associated with climate change (e.g., Wilcox et al., 2012) suggest that there may be very important chemistry-climate feedbacks related to ozone, such as those related to changes in the Brewer–Dobson Circulation (e.g. Hegglin and Shepherd, 2009).

4 Topics

4.1 Megacities

As of 2007 more than half of the world's population now lives in urban areas, and many of them in megacities. This statistic is often cited, but what defines an "urban" area or a "megacity"? While these definitions evolve and differ often depending on the context, here we will consider a common definition of a megacity that is a city or urban agglomeration of greater than 10 million people. As per Parrish et al. (2011), megacities are dense centres of population, economic activity, and pollutant emissions, but also areas where effective pollution control strategies could realize maximum benefit (Parrish et al., 2011). Ground-level ozone is a serious air quality issue in many of the world's megacities. Monitoring and measurement campaigns have documented ozone levels exceeding air quality standards in many megacities. For example, based on the UNECE and WHO guidelines for protection of human health, daily 8 h ozone should not exceed 60 ppb on more than 25 days per calendar year. In Delhi, India this threshold was exceeded approximately 45 days per year on average during the 7 year period (1997–2004), a significant concern for human health in the megacity (Ghude et al., 2008), especially since ozone concentrations there are still on the rise (Chelani, 2012). While some cities have extensive monitoring of ozone (and ozone precursors, more often NO_x than NO_x and NMVOCs), others have limited to no measurements. Buenos Aires, Argentina for example, has very few ozone measurements, so that the overall situation with regard to ozone pollution cannot be thoroughly assessed for the city (Zhu et al., 2012). Sao Paulo, Brazil on the other hand has a more extensive monitoring network and increasing ozone concentrations are observed over the last decade, despite decreases in other pollutants such as NO_x and CO, as well as regular violations of the national ozone air quality standard (Sanchez-Ccoyllo et al., 2006; Zhu et al., 2012). A variety of reported ozone concentrations from megacities are shown in Table 2.

Sources of ozone precursors in megacities include, but are not limited to, traffic-related emissions, combustion of fossil fuels, solvent use, and industrial activities such as power generation. The relative contribution of sources and specific activities leading to the local ozone precursor compound mix varies depending on location, including between cities. For example, in Sao Paulo, Brazil light-duty vehicles are run on ethanol or gasoline/ethanol mix fuels and ethanol from sugar cane accounts for 65 % of all fuel consumed (de Fatima et al., 2012); light-duty vehicles in North America predominantly run on gasoline which in some cases contains a small fraction of ethanol; in China gasoline-powered vehicles dominate the vehicle fleet, but there is also significant use of liquefied petroleum gas (LPG) for some types of vehicles in the fleet (Liu et al., 2008). Overall, the emissions from vehicles/traffic dominate as a major (if not the main) source of ozone precursors in many megacities, especially because growing vehicle fleets generally accompany megacity development (Parrish and Zhu, 2009). For example, Shanghai, the largest city in China with a population of roughly 23 million, has undergone rapid development; between 1996 and 2008 industrial gross output increased by ≈ 4 times and the number of cars increased from 0.47 to 2.61 million (Tie et al., 2013). Other megacities in which vehicles are cited as the top or among the top sources of ozone precursors are Cairo, Delhi, Istanbul, Los Angeles, New York, Mexico City, Sao Paulo, and the Ruhr-Rhein metropolitan region (Chelani, 2012; de Fatima et al., 2012; Parrish et al., 2011; Khoder, 2009; Im and Kanakidou, 2012; Melkonyan and Kuttler, 2012). In cities like Lagos in Nigeria it is a combination of traffic and open biomass burning driving large ozone exceedances from emission of NMVOCS (Marais et al., 2014).

Extreme events in terms of air quality have also been documented in a number of megacities. These result from a combination of elevated emissions and meteorological conditions (e.g., stagnant, hot, sunny) that lead to extremely high concentrations of ozone, typically for a short duration. During the summer of 2010 in Moscow, blocking anticyclonic meteorological conditions with record-breaking high temperatures led to larger than normal evaporative emissions from fuels, paints, etc, as well as emissions from a large number of forest and turf fires, in addition to the "normal" megacity emissions. These conditions which persisted from July through mid-August resulted in maximum hourly mean concentrations of ozone that peaked at 134.2 ppbv (Elansky et al., 2011). An oft cited example of extreme ozone was during the European heat wave during summer 2003, which adversely affect the residents of a number of European megacities. For about 2 weeks at the beginning of August a high pressure system was centred on Western Europe, resulting in record-setting temperatures exceeding 40 °C, and accompanied by a persistent photochemical episode. In France, the highest hourly ozone value reached 417 $\mu g\,m^{-3}$, and concentrations regularly exceeded the EU threshold of 180 $\mu g\,m^{-3}$ (90 ppb) (Lee et al., 2006; Vautard et al., 2005; Stedman, 2004; Tressol et al., 2008).

Because of their high population density, the adverse health effects of elevated ozone levels affect a disproportionately large fraction of the population. A recent study investigated the health impacts of air pollutants in Tehran, Iran where the annual 8 h average ozone concentration in 2010 was 68.84 $\mu g\,m^{-3}$, with a maximum 8 h concentration of 187 $\mu g\,m^{-3}$ during the summer period. The health impact owing to ozone was estimated to cause an excess total mortality of 819 out of 47 284 people in a year, relative to 2194 cases for PM_{10} (Naddafi et al., 2012). For comparison (from a study using the same method), they cited the excess total mortality for PM_{10} was 677 out of 1 308 000 people for Milan, Italy, located in the megacity region of the Po Valley (Naddafi et al., 2012). Cifuentes et al. (2001) assessed the health benefits associated with reductions of PM and O3 from climate change mitigation strategies (2000–2020) in 4 megacities – Santiago, Sao Paulo, Mexico City, and New York. Without going into detail, substantial premature deaths could be avoided from such policies; in all cases the adverse health effects avoided from ozone were significantly less than those from PM (Cifuentes et al., 2001). Generally, small but substantial associations between ozone and total mortality are found in epidemiological studies (Bates, 2005).

The emissions from megacities also have an effect on the surrounding region. In many cases the urban areas have been identified to be VOC-limited, where high NO_x concentrations in the cities suppress ozone concentrations (Im and Kanakidou, 2012; Tie et al., 2013). This suppression of ozone by high NO_x has been identified as generally more characteristic of extratropical megacities in the Northern Hemisphere, relative to tropical cities, because of differences in transport patterns. Tropical cities are more influenced by rapid convective transport, while the extratropical cities allow for a greater build-up of local pollution (Butler and Lawrence, 2009). Local/regional transport of these air masses into the surrounding areas can lead to greater concentrations outside of the megacities. For example, in Tokyo, modelling studies showed that sea breezes developed during the daytime transported emissions from the urban centre to the north, which caused enhanced ozone in downwind areas 50–100 km away (Kondo et al., 2010). Furthermore, regional enhancements of ozone during summer were found in the area (200 km × 200 km) surrounding the Tokyo metro area (Kondo et al., 2010). A modelling study looking at the impacts of Istanbul (and Athens) on air quality in the East Mediterranean also found much lower concentrations of ozone within the (mega)cities owing to significant NO_x emissions depressing O_3. The rural sites in the surrounding area had much higher ozone concentrations, 11–24 ppbv (9–14 ppbv) greater in summer (winter) than in the urban areas, emphasizing the importance of the megacity emissions on regional air quality (Im and Kanakidou, 2012). Further sources of emissions in areas surrounding the megacity regions also play a role in ozone formation. For example, the photochemistry in plumes transported out of London or the Ruhr–Rheine region will be influenced significantly by further emissions sources, while this is much less the case for e.g., Cairo which has far fewer emissions sources in the surrounding area (Hodnebrog et al., 2011). Biogenic emissions will also influence ozone formation downwind of cities. For the Shanghai region, results from a model study suggested that ozone formation was enhanced in the city plumes in the downwind region because of the strongly VOC-limited conditions in the plume which resulted in continuous ozone production during transport. Reasons for this were oxidation of OVOCs and CO in the plume, and biogenic isoprene emissions (Tie et al., 2013). Finally, an estimate of the footprint of southeastern megacities in South America found contributions in excess of 30 % to downwind levels of surface ozone under certain conditions (Zhu et al., 2012).

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Considering ozone concentrations as a relative contribution to the global scale, megacities contribute a surprisingly small amount to global ozone (Stock et al., 2013). In a model "annihilation" experiment where the emissions from grid cells containing megacities were removed, emissions from megacities contributed only 0.84 % to the global average tropospheric ozone column density, proportionally smaller than the 6 % of global anthropogenic ozone precursor emissions from megacities (Butler et al., 2012). This however does not represent human health exposure to ozone in megacities and is also a global average.

Previous work has shown that individual megacities are not well represented by global emission inventories compared to the detailed city-scale inventories (Butler et al., 2012), which can be an issue when trying to model ozone on a larger scale. Additional complexity is added by the non-linearity of the atmospheric chemistry involved in ozone production processes. Hodnebrog et al. investigated the importance of resolution for the representation of large scale tropospheric ozone from megacity emissions and found that higher resolution was much more important for local air pollution studies than for larger climate studies, as might be expected, due to the integration of relatively small changes over a large volume (changes in the resolution of meteorology were not considered) (Hodnebrog et al., 2011). A key point was whether or not the model resolution could capture the NO_x saturated regime within the plume common to many megacities (Hodnebrog et al., 2011). That said, recent work by Siour et al. (2013) has shown that for chemistry transport models, using a "zooming" technique (introducing higher resolution "zooms" to certain areas within a coarser overall resolution) allows for better representation of scale interactions, including better representation of megacity areas, such as the BeNeLux region (Siour et al., 2013). With the growing interest in the study of urbanization, more research and improved methods are still needed to develop a better understanding of pollutants such as ozone in megacities and their effects on all scales.

4.2 Biomass burning

Wildfires/Biomass burning are the second largest source of carbon dioxide emissions, after fossil fuel combustion with ca. 1–2 Gt C year^{-1} (IPCC, 2013). Tropical biomass burning dominates total emissions with boreal fires (50–70° N) accounting for around 9 % of all fire carbon emissions. Burning is thus a major component of the carbon cycle having a direct global impact on climate (van der Werf et al., 2010). Further, there is also an indirect impact because biomass burning is a significant source of ozone precursors (e.g. CO, NO_x, VOCs) and aerosol particles. Indeed, Jaffe and Widger (2012) estimated that global wildfires produce approximately 170 Tg of ozone per year, which is 3.5 % of all tropospheric ozone production. However, as they pointed out, many areas of uncertainty remain in wildfire-related ozone production. These uncertainties centre around the interplay of fire emissions, chemical reactions within the plumes, aerosols effects on chemistry and radiation and atmospheric dynamics (local and downwind meteorological patterns). These factors, along with a strong interannual variability of the fire activity itself, make the assessment of global impact a challenge. The impact of boreal forest fires is less documented and quantified than tropical biomass burning.

Recently, the atmospheric chemistry challenge of biomass burning in Boral regions provided the motivation for the Quantifying the impact of BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites (BORTAS) campaign, held in July–August 2010 and 2011 over Eastern Canada and Western Atlantic. The objective of BORTAS where to better understand the chemical evolution of plumes emitted from the burning of biomass, with a particular emphasis on the net production of tropospheric ozone and downwind impacts on air quality (Palmer et al., 2013 and references therein). Parrington et al. (2013) have shown that ozone formation increases with plume age. They used NMHC ratios (extensively described for this BORTAS campaign in Lewis et al., 2013) to estimate photochemical ages of the observed biomass burning plumes between 0 and 10 days. Parrington et al. (2013) found that Ozone Production Efficiency (OPE) increased with plume ages as calculated by NMHC ratios.

They show $\Delta O_3/\Delta CO$ enhancement ratios increasing from 0.020 ± 0.008 ppbv ppbv^{-1} in plumes with photochemical ages less than 2 days to 0.55 ± 0.29 ppbv/ppbv in plumes with photochemical ages greater than 5 days. According to this study, it seems that the aerosol loading is one of the main driver of such OPE, as aged plumes were typically associated with low aerosol loading and relatively high OPE. In one of the BORTAS flights that made multiple interceptions of a plume with high aerosol loading, Parrington et al. (2013) report that the photolysis rate of NO_2 was reduced by a factor of approximately 2 within this plume, suggesting that increased optical depth of the plume can reduce the photolysis rate of NO_2 to form ozone.

Still in the frame of BORTAS and WMO-GAW programme, results exploring NMVOC ozone precursors from measurements of biomass-burning (Lewis et al., 2013) have suggested that biomass burning can be the largest fractional contributor to observed benzene, toluene, ethene and propene levels in many global locations. The extrapolated widespread biomass burning contribution to atmospheric benzene, a heavily regulated air pollutant, suggesting a pragmatic approach when setting air quality targets as tailpipe and solvent emissions decline in developed countries.

Jaffe and Widger (2012) also indicated that boreal wildfires are likely to produce less NO_x on average than fires in other biomes. This observation makes sense with a more obvious impact of biomass burning on ozone production in the tropics than at mid-high northern latitudes. However, boreal wildfires may have diverse impacts on the global ozone distribution as they are also often linked to convection and pyro-convection allowing thus the injection of ozone precursors and particulate matter up to the upper troposphere-lower stratosphere where long-range transport processes can widely distribute the emissions. Subsequent photochemical processes leading to ozone production and their impact on larger scale may be different than in the tropics. Several groups are actively developing algorithm and models to propose appropriate injections heights for biomass burning emissions (e.g. Kaiser et al., 2012; Freitas et al., 2007). Depending on the fire radiative power (FRP), it is shown that boreal forest fires are likely able to emit products up to 10 km altitude with a maximum between 1 and 4 km altitude for fires with the highest radiative power, while tropical biomass burning is limited to the first km of the atmosphere. Numerous studies report high mixing ratios of biomass burning products, CO in particular, measured in the middle to upper troposphere and eventually up to the lower stratosphere, thousands of km from the fire sources (e.g. Nedelec et al., 2005; Cammas et al., 2009; Fromm et al., 2010; Elguindi et al., 2010). Biomass burning signatures from Canadian forest fires have also been observed in the lower troposphere at the Pico Observatory on the opposite of the North Atlantic (Val Martin et al., 2006). Implications for the ozone budget in Boreal regions are not as direct as in the Tropics. Photochemical impact remains uncertain. Clearly, long range transported biomass burning plumes can influence Europe (Cook et al., 2007; Real et al., 2007) though the impact is variable (Hudman et al., 2004). More recently, European fires in Portugal and Russia have been shown to contribute to air pollution (Tressol et al., 2008; Martins et al., 2012) and the frequency is expected to increase with climate change (Carvalho et al., 2011). Long range transport of biomass burning products from Siberia can influence the west coast of the North American continent (Seattle, Vancouver) and such haze may have strong impact on meeting their air quality standards. Figures 30 summarizes ozone and CO profiles recorded over Vancouver in the beginning of July 2012 recorded in the frame of IAGOS. Further details and profiles may be found on the dedicated MACC web pages: http://www.iagos.fr/macc under the rubric "Profile of the day" in relation to the huge fires in summer 2012. Figure 30 also illustrates the difficulty in assessing the ozone production from such boreal wildfires based on in situ measurements (of limited compounds). Differing profiles over Vancouver have different $\Delta O_3/\Delta CO$ (from almost 0 to 1) and given plume age is increasing everyday (same source, same receptor, same transport pathway apparently). Finally, it is noticeable that the highest ozone concentrations in the lower troposphere are observed on the last day of this time-series.

Biomass burning in the tropics has long been recognized as the major source of tropospheric ozone locally and regionally (Fishman et al., 1990; Thompson et al., 1996, 2003b; Sauvage et al., 2006; Jonquieres et al., 1998). Tropospheric seasonal cycles of ozone are in phase with the local biomass burning season (coinciding with the dry season) of each region. It is worth noting one exception over Equatorial Africa (Gulf of Guinea and adjacent continent) which is impacted by two biomass burning regions, one from each hemisphere. For example, over Lagos, Nigeria, ozone enhanced layers are observed in December–February when burning occurs regionally and also in July–August when biomass burning occurs over southern Equatorial Africa (Sauvage et al., 2005, 2007b). Such processes have been further investigated in the frame of AMMA (Reeves et al., 2010; Thouret et al., 2009; Mari et al., 2008). Similarly, over Brazzaville, the seasonal cycle of ozone peaks in July–August but a secondary maximum appears in January–February due to transport of ozone and precursors from fires occurring in the Northern Hemisphere (Sauvage et al., 2005, 2007b). Thus, the so-called zonal wave-one as described by Thompson et al. (1999) and Sauvage et al. (2006), which describe the ozone maximum over the South Atlantic and adjacent continents clearly designates biomass burning as the main contributor of the ozone burden in the tropical lower to middle troposphere at least. Biomass burning in the tropics may have a global impact too. The extreme El-Nino event in 1997 and the consequent long lasting fires in Indonesia (Siegert et al., 2001) have contributed to the increase of CO and other trace gases (e.g. CO_2) observed globally from late 1997 through 1998.

4.3 Role of biogenics in the formation of ozone

There is much debate as to the influence of biogenic VOCs in urban (Calfapietra et al., 2013), regional and global ozone budgets. Variation in natural plant emissions of ozone precursors can influence ozone concentrations. Goldstein and Galbally suggested we cannot account for the loss of approximately half the non-methane organic carbon entering the atmosphere (Goldstein and Galbally, 2007) much of biogenic origin.

Much of the focus on biogenic VOCs and ozone is on isoprene and the monoterpenes owing to their apparent dominance of the global VOC budgets (see Fig. 21). New insights from field observations, models and quantum chemistry into isoprene chemistry and its impacts have been recently reviewed by Whalley et al. (2014). Some of the new radical chemistry from isoprene oxidation is detailed in Sect. 4.10 and the emissions in Sect. 2.3. This section deals with the relationships between biogenics and formation of ozone.

Work by Hewitt et al. (2011) has suggested that the circadian rhythms of the isoprene emitters have an effect on the ozone budgets (see Fig. 31), but there has been some debate as to the nature of the circadian control (Keenan and Niinemets, 2012).

Model calculations have indicated that the biogenic isoprene emissions represent a major uncertainty in the achievement of AOT40 levels by a factor of at least two (EEA, 2009). The impact of North American (NA) isoprene on European ozone has been assessed and it has been shown that future increases in NA isoprene emissions could offset decreases in EU surface O_3 resulting from controls on NA anthropogenic emissions (Fiore et al., 2011). Archibald et al. (2011) have shown that there is a significant impact of mechanism uncertainties on the global impact of isoprene chemistry on ozone. Recent estimates from Zare et al. (2014) found BVOC to be the most significant contributor to ozone formation over land areas in the NH enhancing the mixing ratio by about 11 %. In the Pearl River Delta in China (Situ et al., 2013) ozone is sensitive to the BVOC levels particularly in urban areas. At a regional European scale, biogenic emissions increase O_3, locally, while reducing $PM_{2.5}$ levels (Tagaris et al., 2014). At the city scale, modelling has shown that O_3 concentration can be increased by 37 ppb in Seoul, Korea owing to biogenic isoprene emission and transport of it key oxidation products into the metropolitan area (Lee et al., 2014).

The role of isoprene nitrates has been highlighted as a key uncertainty in ozone and NO_x chemistry (Horowitz et al., 2007). In the tropics regional simulation of ozone is shown to be very sensitive to the removal and export of NO_x by isoprene nitrates (Paulot et al., 2012). For example, in South America and New Guinea, the high ratio of isoprene to-NO_x emissions makes isoprene nitrates chemistry the primary sink of NO_x. Paulot et al. (2012) suggest that the impact of isoprene photooxidation on tropical ozone is not limited to the regional scale but can have a long-range effect as a result of dynamic and photochemical processes such as efficient vertical mixing (through deep convection) and low boundary layer HO_x (as a result of high biogenics and low NO_x emissions). It is suggested that these physical and chemical conditions, promote the oxidation of isoprene outside of the boundary layer, where its contribution to ozone production is amplified (Paulot et al., 2012). Enhancing the isoprene oxidation mechanism for isoprene-nitrates in a global model and running it over the USA, Mao et al. (2013) have shown that the dependence of surface ozone on isoprene emission is positive throughout the US, even if NO_x emissions are reduced by a factor of 4, as well as the chemistry leading to the export of nitrates to the background atmosphere. Browne et al. (2014) have shown that the monoterpene nitrates have the potential to impact ozone levels over the remote continental boundary layer. The change in global O_3 burden due to an increase in BVOC emissions associated with temperature depends critically on the assumed treatment for the fraction of NO_x recycled from isoprene nitrates (Ito et al., 2009).

There is significant debate about the role of a wide range of biogenics in ozone chemistry under future climate e.g. (Andersson and Engardt, 2010) with up to a factor five difference between different models for Europe (Langner et al., 2012b). A limiting role of increased CO_2 on the potential of ozone precursor emissions from the vegetation has been recently noted at the global scale (Lathiere et al., 2010). Earlier studies showed that the vegetation response to climate change is important in driving BVOC emissions and subsequent formation of ozone (Sanderson et al., 2003).

Several other studies have focused only on the regional impact of climate change (Langner et al., 2012a, b; Andersson and Engardt, 2010; Manders et al., 2012; Hedegaard et al., 2008, 2013; Katragkou et al., 2011). They found a general increase of ozone concentrations owing to increasing biogenic emissions and favourable conditions for the build-up of ozone pollution as a result of increased temperature, more frequent summer blocking and heat waves and increased shortwave radiation. Whereas all these studies agreed on the main outcome of climate change on ozone in Europe, they also pointed out significant differences depending on the regional climate model used. The main factors influencing these differences are the projections of cloud cover and frequency of stagnation episodes that are highly variable across the ensembles of regional climate projections.

4.4 Halogens

Halogens (chlorine, bromine, iodine) influence the concentrations of ozone in the troposphere either directly, by reacting with O_3 itself (e.g., $Br + O_3 \rightarrow BrO + O_2$), or indirectly, by affecting its sources and sinks. Indirect influence results in production or destruction of O_3, depending on the conditions. Halogens, especially chlorine, react with VOCs to form peroxy radicals, which convert NO into NO_2, and change the OH/HO_2 ratio (e.g., via $BrO + HO_2 \rightarrow HOBr + O_2$, followed by HOBr photolysis to give OH). Reactions between halogen species and nitrogen oxides also affect the NO/NO_2 ratio, and form stable compounds, which can act as nitrogen reservoirs and allow long-range transport of O_3 precursors. A detailed model analysis by Saiz-Lopez et al. (2012a) estimated that halogens are responsible for up to 10 % yearly depletion of the total tropospheric O_3 column (and up to 20 % in the tropical troposphere), especially in the middle and upper troposphere. The model calculations by Parrella et al. (2012) and Long et al. (2014) generally agree with these estimates. The Long et al. (2014) model analysis suggest that models may overestimate the role of bromine (and the extent of ozone destruction), because they tend to overestimate marine aerosol, especially in the Southern Hemisphere.

Our understanding of the role of halogens in ozone chemistry ultimately depends on our understanding of the physio-chemical processes that release, transform and destroy halogen species into the atmosphere. There are significant uncertainties in our knowledge of the source processes and geographical distribution of halogens and severe limitations in the databases of chemical kinetics parameters (Abbatt et al., 2014). Part of the problem is related to the difficulty in measuring halogens species at the low concentrations found in the atmosphere (Finlayson-Pitts, 2010): this area of research has been very active in recent years and many of the most recent advancements in our knowledge are related to developments in the field of analytical chemistry, particularly mass spectrometry.

Very detailed reviews have been published in recent years both on halogen chemistry in general Saiz-Lopez and von Glasow (2012) and on specific aspects of halogen chemistry, such as bromine (Sander et al., 2003), iodine (Saiz-Lopez et al., 2012b; Carpenter, 2003) and polar chemistry (Simpson et al., 2007). These reviews detail the broader picture of halogen chemistry and the focus hereafter will be on recent advances that directly affect tropospheric ozone.

Overall, observations of halogen species in the boundary layer show a consistent picture across the globe (see Saiz-Lopez and von Glasow, 2012), with comparable levels of reactive halogens in different unpolluted/semi-polluted regions, and more variable levels of reactive halogens in continental/coastal environments, reflecting the larger variability in their sources and sinks under polluted conditions.

The major source of chlorine and bromine in the boundary layer is known to be sea-salt: current model parameterizations are able to reproduce measured BrO levels in the unpolluted MBL reasonably well (Keene et al., 2009; Sommariva and von Glasow, 2012; Saiz-Lopez et al., 2012a). However, models struggle to reproduce total bromine and particulate bromide concentrations and their diurnal cycles, suggesting that our understanding may be limited by the lack of speciation of bromine in current analytical techniques.

Inorganic chlorine observations are better constrained, although concurrent measurements of Cl_2 and HOCl, especially under semi-polluted conditions (Keene et al., 2009; Lawler et al., 2009, 2011), are difficult to reconcile and BrCl, which the models predict as one of the major components of total Br, has not been detected in marine environments. It is unclear whether the models-measurements disagreements are due to instrumental issues or to some fundamental problem in our understanding of the chemistry, particularly in the aqueous phase (Long et al., 2014; Sommariva and von Glasow, 2012), but they make it difficult to accurately assess the effect of chlorine and bromine on ozone under unpolluted and semi-polluted conditions.

In the past few years, several groups have reported observations of significant concentrations of $ClNO_2$ (from 80 ppt to over 2000 ppt) in a variety of environments and under different conditions (Osthoff et al., 2008; Kercher et al., 2009; Thornton et al., 2010; Mielke et al., 2011, 2013; Phillips et al., 2012; Riedel et al., 2012, 2013; Wagner et al., 2012). These studies indicate that nocturnal formation of $ClNO_2$, via reaction of N_2O_5 with aerosol chloride, followed by its photolysis at sunrise to form $Cl + NO_2$ is a strong and widespread source of reactive chlorine in the polluted troposphere. In addition, to kick starting VOC oxidation in the morning before the formation of OH, the $ClNO_2$ mechanism also acts as a NO_x reservoir, preventing NO_2 loss overnight as HNO_3 and hence making it available in the morning to form O_3. Although these two effects are not yet fully decoupled and understood (see discussion in Young et al., 2014), it is clear that this chemistry is potentially very important for ozone formation in polluted environments. Osthoff et al. (2008), Thornton et al. (2010) estimated that up to 13 ppb additional ozone can be formed via this chemistry. It must be noted, however, that the actual impact on local ozone may be much less than that, because of the effect of transport and local circulation on ozone levels (Sarwar et al., 2012; Simon et al., 2009, 2010). Furthermore, model analysis suggests that recirculation of air masses from urban coastal areas over the ocean may lead to high Cl_2 levels during the night, thus increasing VOC oxidation and ozone formation at sunrise (Pechtl and von Glasow, 2007), a mechanism which has particular relevance for coastal megacities.

There are several inconsistencies in the observations of reactive iodine, especially under conditions representative of the open ocean: for example, Carpenter et al. (2010) highlighted the discrepancy between observations of IO made by different groups at the Cape Verde islands, while Mahajan et al. (2010), found that IO concentrations in the eastern Pacific did not agree with the observations of Chlorophyll *a* and Dissolved Organic Matter and were much lower than the SCIAMACHY satellite observations. Additionally, the measured emission rates of iodinated VOCs are unable to explain the observed levels of IO and I_2 (Carpenter et al., 2013; Jones et al., 2010b; Grossmann et al., 2013; Lawler et al., 2014). Several mechanisms have been introduced to explain the observations and are still under active discussion (e.g., Lawler et al., 2014; Carpenter et al., 2013; MacDonald et al., 2014). Some of these discrepancies may be explained by assuming seasonal or yearly cycles of the iodine sources, but there are also several uncertainties in the iodine chemical mechanism (Sommariva et al., 2012; Saiz-Lopez et al., 2012b). The many uncertainties in iodine sources and chemistry make it difficult to assess accurately the role of iodine as ozone sink in unpolluted/semi-polluted conditions, especially over the open ocean. Although the sources and chemistry of iodine species are still being debated, it is well established that iodine species do not react with VOC and, when NO_x levels are high, they form stable iodine nitrates (INO_x) which can be taken up on aerosol, leading to net loss of NO_x (and hence O_3). In addition, recycling of INO_3 in the gas-phase ($INO_3 + I \rightarrow I_2 + NO_3$) may increase ozone depletion by up to 60 % (Mahajan et al., 2009).

The interaction between iodine and ozone also leads to the formation of ultra-fine particles under certain conditions (e.g. coastal regions with strong emissions of iodine from macro-algae, McFiggans, 2005), although this process, and its impact on local O_3 concentrations, is not yet completely understood. Recent work has shown increased O_3 deposition velocities during low tides, owing to direct deposition to macro-algae and/or to a O_3 involvement in iodine-mediated particle formation (McFiggans et al., 2010).

All recent observational and modelling studies of halogen chemistry generally agree that reactive halogen species are present in the unpolluted/semi-polluted marine boundary layer at levels that result in significant depletion of tropospheric ozone and loss of O_x. Read et al. (2008), Sommariva and von Glasow (2012) and Saiz-Lopez et al. (2012) calculated the contribution of halogens to ozone destruction using different models. The results, varying from 3 to 14 ppb per day, indicate that halogens overall are the second most important sink for Ox in unpolluted and semi-polluted conditions, accounting for up to a third of total ozone loss in the tropical troposphere (Fig. 32). Bromine is about twice more important than chlorine as ozone sink, and iodine is potentially more efficient than bromine although its concentration shows a steeper vertical gradient, making it less important than bromine and chlorine above 500–600 m (Sommariva and von Glasow, 2012). It must also be noted that the co-presence of iodine and bromine makes the loss of ozone more efficient than if bromine alone were present, due to the multiplying effect of inter-halogens reactions (e.g., IO + BrO, Read et al., 2008). In polluted regions, owing to the higher concentrations of NO_x, the oxidation of VOC by Cl and, to a lesser extent, Br, results in net ozone production. For example, Finley and Saltzmann (2008) calculated that the levels of dihalogens (up to 26 ppt of Cl_2 and up to 9 ppt of Br_2) observed in California could account for up to 10 % of measured ozone.

The role of halogens in the boundary layer is likely to be impacted, and possibly become even more relevant for O_3 photochemistry, by changes in the Earth System, which may alter the formation of marine aerosol, as well as increased emissions of acids and acid precursors, which affect the halogen activation processes (Long et al., 2014).

At polar latitudes (> 60°), periodic ozone depletion events (ODE) have been observed since the mid-1980s and have been linked to bromine release from the snowpack (Simpson et al., 2007) with observed BrO levels ranging from 5 to 41 ppt (Roscoe et al., 2014; Saiz-Lopez and von Glasow, 2012). Recently, novel observations of BrO (Liao et al., 2011) have shown that "BrO clouds" tend to be distributed homogeneously over scales of a few km during ODE, while Salawitch et al. (2010) found that BrO columns are correlated with the height of the tropopause, although some "hotspots" are related to free tropospheric or stratospheric intrusions.

There is much less information regarding iodine and chlorine in Polar Regions. Chlorine presence has been inferred only by VOC ratios in the past; recently Pohler et al. (2010) and Liao et al. (2014) have reported the first observations of OClO (up to 24 ppt) and Cl_2 (up to 100 ppt), respectively, in the Arctic. These findings suggest that Cl may enhance O_3 depletion in the Polar Regions, mostly via its close coupling with bromine chemistry (with the ClO + BrO reaction contributing up to 73 % to ozone depletion). Iodine species (IO) have been detected in Antarctica at levels comparable to BrO (∼ 20 ppt, Saiz-Lopez et al., 2008), which increase O_3 loss rate by up to 3 times.

Only one study reported IO in the Arctic at < 3.4 ppt (Mahajan et al., 2010); whether this is due to differences between the two polar regions (e.g., biological communities or sea ice characteristic) is at present unclear.

Many questions remain on the mechanism of release of chlorine/bromine species from the snowpack (see Abbatt et al., 2012 for a detailed review). An important issue is whether it can explain observed HO_x and NO_x levels (Saiz-Lopez et al., 2008; Bloss et al., 2010), as well as observed halogens levels. A modelling study by Thomas et al. (2011), indicated that up to 10 ppt of tropospheric BrO can be explained by a mechanism involving nitrate formation in the interstitial snow; if this is the case, the resulting formation of NO_x may compensate the depletion of O_3 owing to reactive Br, possibly leading to net ozone formation. Additionally, since bromine release is connected with first-year sea ice (Saiz-Lopez and von Glasow, 2012), changes in sea ice formation due to climatic change are likely to affect ozone photochemistry significantly.

The importance of localized sources of halogens, such as salt lakes, salt beds, saline soils and marshes, for O_3 photochemistry is at present unclear. Large concentrations of bromine and iodine (up to 200 ppt of BrO, Tas et al., 2005, and up to 10 ppt of IO, Zingler and Platt, 2005) have been reported over the Dead Sea (Israel) causing O_3 as low as 2 ppb; however, observations in other locations have shown much lower values (e.g., 6 ppt of BrO and 15 ppt of ClO over the Great Salt Lake, Stutz et al., 2002). The database of observations is very sparse and shows large variability between different locations, suggesting that the local characteristics (e.g, latitude, pH, geology, ecosystem and local meteorology) of the salt lakes are crucial in determining the strength of halogen emissions and therefore of the magnitude of the ODE they trigger (Smoydzin and von Glasow, 2009).

Chlorine and bromine species have also been detected in volcanic plumes at ppm and ppb levels, respectively (Saiz-Lopez and von Glasow, 2012), leading to ozone depletion inside the plume which can persist for at least 3 days and possibly longer (see (von Glasow, 2010), for a detailed discussion). Similar chemistry may be expected from other types of volcanic activity, such as volcanic fields, vents, fumaroles, etc. . . and may affect ozone levels both in the boundary layer and in the free troposphere. The extent to which halogens from volcanic activity affect ozone photochemistry on a larger (regional/global) scale depends on several variables, including the type, frequency and extent of volcanic activity, the mixing with the background air and the synoptic circulation.

Besides the injection of halogen species by volcanic activity (see above), the main sources of halogens in the free troposphere are believed to be the oxidation of halocarbons, the uplift of aerosol and stratospheric intrusions (Saiz-Lopez and von Glasow, 2012), although direct observations are scarce. Pommier et al. (2012) found evidence of biomass burning from Siberian fires as a source of BrO (> 5 ppt) in the Arctic free troposphere, although the release mechanism is unclear; Roscoe et al. (2014) compared ground based and remote sensing measurements in Antarctica and concluded that they could only be reconciled by assuming large amounts of BrO at high altitudes, in broad agreement with the findings by Koo et al. (2012).

Jones et al. (2010a) found a strong association between high altitude ODEs and atmospheric low pressure systems which drive the formation of large scale BrO clouds over Antarctica. Free troposphere-boundary layer dynamic may also be important outside the Polar Regions. For example, Long et al. (2014) suggested that the accumulation of insoluble bromine in the free troposphere (via sulphur oxidation by HOBr and/or HBr condensation on aerosol) may explain the observed Br enrichment of submicron aerosol after entrainment of these species back in the boundary layer. These recent findings suggest the presence of large concentrations of inorganic Br at high altitudes in the troposphere and model calculations show that they may account for 3–15 % reduction in tropospheric O_3 (von Glasow and Crutzen, 2004). Lary (2005) has examined the role of halogens in the free troposphere using chemical data assimilation technique and concluded that chlorine and bromine can affect significantly the levels of methane (10–50 % of the total oxidation rate) and ozone in the upper troposphere, especially at polar and tropical latitudes.

Recently, IO has also been observed in the tropical and sub-tropical free troposphere at concentrations between 0.2 and 0.4 ppt (Dix et al., 2013; Puentedura et al., 2012). Assuming 0.5 ppt of BrO and 0.6 ppt of IO, Dix et al. (2012) estimated that iodine accounts for 11 and 26 % of total ozone loss in the free troposphere and in the boundary layer-free troposphere transition region, respectively.

4.5 Tropospheric ozone and global perturbation of the nitrogen cycle

The drivers of enhanced tropospheric ozone are emissions of the precursors, NO_x and VOC, and viewed globally the hot spots for ozone production coincide with the areas of largest NO_x emissions (Stevenson et al., 2006), most notably in Europe, North America and Asia. Thus the effects of elevated tropospheric ozone are coupled to anthropogenic emissions of NO_x, an important anthropogenic contribution to the current global cycling of fixed nitrogen (Nr), to distinguish it from the atmospheric reservoir of unreactive N_2. Recent assessments of the global nitrogen cycle have quantified the major natural and anthropogenic fluxes of Nr (Sutton et al., 2011; Galloway et al., 2004). The scale of the human perturbation of the global nitrogen cycle is substantial, with approximately half of the 413 Tg N annual fixation of atmospheric nitrogen into reactive oxidized NO_y and reduced, NH_x forms (Fowler et al., 2013b) contributed by anthropogenic activities (Lu et al., 2013). Within this total, most of the nitrogen fixed annually is by industrial production of ammonia in Haber–Bosch industrial plants and within soils and oceans by microbial processes. Only a small fraction of this Nr is emitted to the atmosphere (see Fig. 33). The emissions most important for tropospheric ozone production are of NO_x from combustion, in vehicles and industry, which totals approximately 40 Tg N annually, just 10 % of total Nr production.

While the focus of this review is tropospheric ozone, it is important to recognise the wider impacts of the human perturbation of the nitrogen cycle (Fowler et al., 2014). These include eutrophication of terrestrial and marine ecosystems, reductions in biodiversity of terrestrial ecosystems over Europe and North America, widespread effects on human health from the aerosols containing nitrogen compounds and radiative effects on global climate and reductions in stratospheric ozone from elevated N_2O emission, as detailed by Erisman et al. (2013). The negative effects of contamination of the environment by nitrogen compounds has been extensively documented for Europe (Sutton et al., 2011) and North America (Suddick et al., 2013). However, evidence from Asia and especially China and India is increasing rapidly and the absolute values for deposition of Nr in these regions are among the largest globally and effects on ozone production and terrestrial eutrophication are widespread.

Relatively little research on the effects of nitrogen emission has been reported for in tropics, but new evidence from work in SE Asia by Hewitt et al. (2009) suggests that these regions are very sensitive to emissions of NO_x which are projected to increase substantially over coming decades as natural rainforest ecosystems are replaced by agriculture e.g. plantations of oil palm.

One of the distinctive features of the nitrogen cycle is the rapid transformation of nitrogen compounds within, and transfers between the atmosphere, vegetation, soils, fresh and marine waters. Thus emissions of oxidized nitrogen to the atmosphere are rapidly oxidized and deposited into terrestrial ecosystems, where it may be transformed into amino acids and subsequently decomposed to ammonium following decay and returned to the atmosphere as ammonia. In the processes within this short sequence, the NO_x in the atmosphere may have generated ozone, reduced the lives of humans breathing NH_4NO_3 containing aerosols and contributed to species loss in terrestrial ecosystems. The same emitted N atom may have contributed to a series of different effects within the Earth system before it is returned back to the atmospheric reservoir as N_2 following denitrification in soils or within the ocean. This effect has been referred to as the nitrogen cascade (Galloway et al., 2003) and shows a very large range of effects of reactive nitrogen on climate, terrestrial and marine ecosystems and on human health. A full analysis of the global effect of nitrogen has yet to be completed, but assessments have been recently published for Europe (Sutton et al., 2011) and for North America (Suddick et al., 2013).

One further aspect for consideration is the coupling between tropospheric ozone, carbon uptake in the terrestrial biosphere and nitrogen (Simpson et al., 2014). It has been recently shown that limitations of available nitrogen for sufficient plant growth reduce the negative impact of tropospheric ozone on carbon uptake in plants, leading to a smaller indirect change in radiative forcing than previously calculated (Kvalevåg and Myhre, 2013).

4.6 Challenges in modelling ozone

Models are the integrator of the chemical and physical knowledge with respect to ozone in the atmosphere. They are much relied on for analysis of observational data, hindcasting, policy support and forecasting across a range of temporal and spatial scales. Models vary much in scale, resolution and with physical/chemical complexity.

With respect to current global ozone, Young et al. (2013) compared modelled (ACCMIP models) and observed (ozone-sonde and satellite (OMI/MLS)) present-day spatial distributions and seasonality of global tropospheric ozone. The models captured the seasonality well at most locations. Based on the comparison to OMI/MLS data the models typically overestimated annual mean tropospheric column ozone at 0–50° N by ≈ 0–30 % and underestimate it at 0–50° S by ≈ 0–25 %. Similarly, re-analysis model data for ozone from MACC shows biases of −5 to +10 % with respect to ozonesondes and aircraft data in the extratropics, but with larger negative biases in the tropics (Inness et al., 2013). These results indicate that models don't fully represent the processes controlling the present-day ozone distribution.

Parrish et al. (2014) have shown that three of the ACCMIP models, driven by trends in emissions, underestimate observed trends in surface ozone over the period since ∼ 1950, at NH mid-latitudes; similar results have been found earlier, e.g. (Schultz et al., 2007b). Cooper et al. (2014) extended this analysis to show that models also underestimate trends in other regions. These observations suggest that modelled ozone appears to be rather too insensitive to emissions perturbations (or possibly that historical emissions changes are not well described, see Sect. 2.3). Emissions remain a key uncertainty for global models (Frost et al., 2012).

Hess and Zbinden (2013) and Hess et al. (2014) find that the evolution of stratospheric ozone, and how this ozone is transported into the troposphere, is a major determinant of historical inter-annual variability of NH mid-latitude ozone throughout the troposphere, and may have significantly contributed to long-term trends. This work indicates that global models need a detailed representation of stratospheric and UT/LS processes in order to simulate ozone trends and variability correctly.

Further challenges to models include, the representation of different aspects of ozone chemistry (e.g., isoprene: Archibald et al., 2010; Dunker et al., 2014; halogens: Yang et al., 2005; Saiz-Lopez et al., 2012a; chemical mechanism, Saylor and Stein, 2012) and deposition (Val Martin et al., 2014). For models to represent many of these processes, adequate resolution is required (Colette et al., 2014).

A couple of studies (Wu et al., 2007; Wild, 2007) have argued that much of the variance in ozone production across models can be explained by differences in NO_x emissions, inclusion of nonmethane volatile organic compounds (NMVOCs, mostly biogenic isoprene) and ozone influx from stratosphere–troposphere exchange. Model tagging offers insights into separating processes such as transport and chemistry (see e.g. Garny et al., 2011).

The challenge for global modellers is prioritising and including all relevant processes in a model with sufficient resolution and while keeping it sufficiently computationally efficient so that it can be useful for a wide range of studies.

A large range of models are used to address ground-level ozone at the regional scale (Kukkonen et al., 2012). Taking into account only emission control policies for the present or near future (2010 or 2020), several multi-model exercises have been conducted in support to the Clean Air For Europe programme (CAFE). The CityDelta project (Cuvelier et al., 2007) aimed to predict the impact and uncertainty of emission reductions of several emission scenarios for 2010 in several European cities. The same exercise was carried out at the larger scale of the European continent (EuroDelta:

van Loon et al., 2007). At continental scale the efficiency of emission reductions was demonstrated but models provided a large spread of responses in city centres. The ability of an ensemble of six chemistry transport models to capture recent observed ozone trends was also discussed by Colette et al. (2012). They found that models efficiently captured the increase in NO_x saturated areas, such as the Benelux region and the decrease in NO_x limited areas (many rural regions in Europe). The quantitative skill of the model was however difficult to retrieve owing to the lack of significant trends throughout Europe over the period selected for the experiment. They also emphasized that modelled trends where highly sensitive to the trends in precursors prescribed in the inventory which exhibited some significant inconsistencies compared to observations of NO_2, in particular.

A regional model comparison of ozone is shown in Fig. 34. The comparison found that no one model was the "best" model on all days, indicating that no single air quality model could currently be relied upon to inform policymakers robustly in terms of NO_x- vs. VOC-sensitivity. For this reason coupled to basic statistical arguments, it was argued that it is important to maintain diversity in model approaches (Derwent et al., 2014).

With respect to regional models Kukkonen et al. (2012) have highlighted the most prominent gaps of knowledge for chemical weather forecasting models; these include emission inventories, the integration of numerical weather prediction and atmospheric chemical transport models, boundary conditions and nesting of models, data assimilation of the various chemical species (see e.g. Gaubert et al., 2014), improved understanding and parameterization of physical processes, better evaluation of models against data and the construction of model ensembles.

It is clear that next generation models will push to greater resolution on the regional scale (Colette et al., 2014).

4.7 Lightning

Globally, lightning flashes occur about 50 times per second, equal to 4.3 million times per day and roughly 1.5 billion times per year. Lightning flashes dissociate N_2 molecules, leading to NO production (Schumann and Huntrieser, 2007), a key source of NO_x in much of the troposphere, especially the tropical upper troposphere (Schumann and Huntrieser, 2007; Grewe, 2008; Grewe et al., 2012; Levy et al., 1996). More than 80 % of summertime upper tropospheric NO_x above the eastern United States is produced by lightning (Cooper et al., 2009) and can be significant contributor to surface ozone (Hudman et al., 2009). Lightning NO_x (NO_2) has been detected from space (Beirle et al., 2010; Choi et al., 2005). The lightning produced NO perturbs atmospheric composition in several ways relevant to climate, as NO is an important determinant of OH/HO_2 ratios via the reaction:

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (R3)$$

The NO_2 photolyses to release an oxygen atom that can go on to form ozone:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (R1)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (R2)$$

Given sufficient UV radiation and a supply of HO_2, NO_x will efficiently generate O_3 (see Sect. 2.1.1). Figure 35 shows modelled contribution of individual sectors in terms of NO_x emissions, including lightning, to the tropospheric ozone column (Grewe et al., 2012). Toumi et al. (1996) highlighted that O_3 production from lightning NO_x (L_{NO_x}) may represent an important positive climate feedback, if a warmer world generates more lightning (Reeve and Toumi, 1999).

However, in addition to leading to O_3 production, Reaction (R3) enhances OH. This increases the methane removal via the reaction:

$$CH_4 + OH + O_2 \rightarrow CH_3O_2 + H_2O \qquad (R11)$$

shortening the CH_4 lifetime, and hence reducing its atmospheric concentration, exerting reducing radiative forcing (RF) (e.g. Derwent et al., 2001; Wild, 2007; Wild et al., 2001).

Enhanced levels of OH will tend to increase production of all secondary aerosols (e.g., including sulphate), which would increase the magnitude of the negative radiative forcing owing to aerosols (e.g. Stevenson et al., 2005).

The catalytic cycle of O_3 production described by Reactions (R1)–(R3) is terminated when NO_x is removed by the reaction:

$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{R12}$$

This and other analogous reactions produce various forms of nitrates, including nitrate aerosol. Enhanced levels of nitrate aerosol, which typically scatters solar radiation, will exert a negative RF (e.g. Shindell et al., 2009), although specific studies of nitrate aerosol associated with L_{NO_x} are apparently lacking.

Any perturbations to NO_x (including lightning) will potentially lead to climate feedbacks via the biosphere, through deposition of NO_3 and O_3, and impacts on the carbon cycle (e.g. enhanced or reduced uptake of CO_2 by vegetation; Sitch et al., 2007; Felzer et al., 2007). It is unclear if the net effect on CO_2 would result in a positive or negative RF.

Most studies suggest more lightning (NO_x) in a warmer world (Schumann and Huntrieser, 2007; Williams, 2005; Banerjee et al., 2014), but these are typically based on the Price and Rind (Price and Rind, 1992) parametrization that links L_{NO_x} emissions to cloud top height (raised to the power 4.9 over land; to a lower power over ocean). Other parametrizations link L_{NO_x} emissions to cloud ice (see e.g. Finney et al., 2014; Tost et al., 2007), and as warming increases, ice declines, and so does L_{NO_x} (Jacobson and Streets, 2009). In addition, some schemes relate L_{NO_x} to aerosols (Yuan et al., 2012; Venevsky, 2014), with potentially complex links between climate and L_{NO_x}. With global warming, tropical stability increases (Held and Soden, 2006; Chou et al., 2013) tending to reduce convection. However, the tropopause tends to rise, allowing convection to reach greater heights. In the Price and Rind (1992) scheme, the higher tropopause affect typically dominates, although there can be regional increases/decreases in some models (e.g., Stevenson et al., 2005).

In summary, the literature suggests that L_{NO_x} increases lead to higher levels of O_3, OH, nitrate, and secondary aerosols in general, but less CH_4, and have unknown impacts on CO_2. It remains unclear if the net impact of increases in L_{NO_x} on climate is warming or cooling; it is also unclear if L_{NO_x} represents a positive or negative climate feedback.

4.8 Arctic

The Arctic is under-going rapid change as a result of global warming. This can, in part, be attributed to production of ozone from tropical and mid-latitude emissions of ozone precurors, especially methane. Climate change together with economic drivers, is also opening up the Arctic to new sources of pollution, such as shipping or oil/gas extraction which may lead to siginificant local or regional increases in surface ozone and associated impacts on Arctic air quality and deposition to fragile ecosystems (Law and Stohl, 2007).

Observed Arctic O_3 mixing ratios vary between 20 and 40 ppbv at the surface and increase with altitude up to the tropopause (8–10 km) (Hirdman et al., 2010). Even though annual data on Arctic O_3 is rather limited, significant differences can be seen in the seasonal cycle at different locations, driven by both remote and local processes (see Fig. 36) (Hirdman et al., 2010). Certain sites, such as Barrow (Alaska) or Alert (Canada), show evidence of halogen influenced depletion during the spring months. As discussed in Sect. 4.4, halogen chemistry over sea-ice or snow covered regions can lead to very low or even near-zero O_3 concentrations near the surface in the Arctic spring (e.g. Barrie et al., 1988). Other sites, such as Zeppelin, exhibit a spring maximum. Higher concentrations in the spring appear to be due to O_3 formation from precursors related to the breakdown of Arctic Haze at this time of year in the lower and middle tropopshere (Emmons et al., 2003). Arctic Haze builds up during the winter each year as a result of transport of mid-latitude pollution into the polar dome (e.g. Barrie et al., 1981) and contains elevated levels of O_3 precursors (CO, VOCs, NO_x) as well as PAN, an important source of NO_x (e.g. Hov et al., 1989).

Summit, which is at a higher elevation (3 km), on Greenland, has a late spring/early summer maximum, likely owing to transport of polluted air masses, primarily from North America, but which could also include a contribution from snow NO_x emissions (e.g. Grannas et al., 2007) or from the stratosphere. There are indications that O_3 concentrations continue to increase in the Arctic both at the surface and at higher altitudes in the troposphere. Hess and Zbinden (Hess and Zbinden, 2013) reported an increasing trend in the European Arctic middle troposphere (500 hPa) of $0.36 \pm 0.23\,\mathrm{ppb\,yr^{-1}}$ from ozonesonde measurements over the period 1996–2010, and Oltmans et al. (2006, 2013) reported a trend of $0.87 \pm 0.50\,\%\,\mathrm{yr^{-1}}$ from surface measurements in 1992–2004 at Alert in the Canadian Arctic.

Several studies have examined sources of pollution transported to the Arctic. In a multi-model assessment, Shindell et al. (2008) examined precursor emission sensitivities to emissions from different mid-latitude source regions on the Arctic and found, for example, European CO emissions to be important in the winter. However, surface Arctic O_3 in winter was most sensitive to European NO_x owing to the domination of strong titration (O_3 removal) in air masses. This was also confirmed by Hirdman et al. (2010). Emissions from Asia and Europe have been found to be important sources of Arctic O_3 in spring in the free troposphere together with stratospheric injection although relative contributions vary between studies and years (Wespes et al., 2012; Shindell et al., 2008). Wespes et al. (2012) found that European anthropogenic emissions were important for lower tropospheric summertime Arctic O_3 in contrast to a previous study (Shindell et al., 2008). Production of O_3 from PAN decomposition in air masses transported from mid-latitudes has also been identified as an important source of Arctic tropospheric ozone in the summer months (Walker et al., 2012). Indeed, aircraft observations collected during POLARCAT-IPY show elevated PAN and CO concentrations in air masses transported from Asian and North American anthropogenic emission regions in summer 2008 (Law et al., 2014 and references therein). Boreal forest fires are also an important source of PAN and, due to their proximity to the Arctic, plumes can be transported to high latitudes during the spring and summer months (Brock et al., 2011; Singh et al., 2010). Whilst little O_3 production appears to occur close to boreal fires (Alvarado et al., 2010; Paris et al., 2010), several recent studies have shown O_3 production downwind from boreal fires in the Arctic during the summer months (Wespes et al., 2012; Parrington et al., 2012; Thomas et al., 2013). Nevertheless, O_3 production is higher in air masses influenced by anthropogenic emissions.

However, global and regional models still struggle to capture vertical distributions of trace gases, including ozone in the Arctic. CO concentrations are often underestimated even in multi-model simulations carried out as part of the POLARCAT model inter-comparison project (POLMIP) using the same emission datasets (Monks et al., 2014; Emmons et al., 2014). Discrepancies appear to be related to either differences in oxidative capacity (OH) or vertical transport of pollutants from mid-latitude source regions into the Arctic. Modelled concentrations of NO_y species such as PAN or HNO_3 also show large variability and siginificant discrepancies compared to measurements (Arnold et al., 2014) pointing to lack in our understanding about chemical processing in polluted air masses transported to the Arctic (Law et al., 2014).

As a short-lived climate forcer, tropospheric O_3 contributes to Arctic warming. For example, Shindell et al. (2006) estimated that anthropogenic emission increases since 1900 could be responsible for 25 % of surface temperature changes in the Arctic. Shindell (2007), based on the results from one model, estimated that about 50 % of the Arctic radiative forcing owing to ozone may be coming from O_3 produced at mid-latitudes (impacting poleward heat transport) and about 50 % from ozone produced in the Arctic. New local sources of pollution may also impact Arctic O_3 in the future such as increased emissions from shipping (Granier et al., 2006) or oil and gas production. Dalsøren et al. (2013) examined impacts of future shipping on radiative forcing in the Arctic and found, particularly in the high-end scenario (from Corbett et al., 2010), that

O_3 radiative forcing from shipping is important in the summer and transit season (May to October) when sea-ice is at a minimum.

4.9 Unconventional oil and natural gas production: “fracking” and air quality

Fossil fuel energy production is rapidly transforming and expanding owing to unconventional oil and natural gas extraction techniques, with implications for regional-scale ozone production. Unconventional oil and natural gas is extracted from tight geological formations (such as sandstone, coal and shale) through the use of hydraulic fracturing (also known as fracking) and directional drilling (Field et al., 2014; Bickle, 2012). These techniques allow wells to be drilled vertically into a shale formation and then horizontally through the formation, after which a mixture of water, sand and chemicals is pumped into the well at high pressure, fracturing the rock and allowing oil and gas to escape.

In the USA, the most extensive extractors of unconventional gas/oil, the shale plays (a name for the deposits) are located in many large basins across the country, primarily in the Rocky Mountains, Great Plains and the Appalachian Mountains. In terms of natural gas, the most productive shale plays are the Marcellus Shale (West Virginia, Pennsylvania, New York) (Kargbo et al., 2010) and the Haynesville–Bossier Shale (Texas and Louisiana). The greatest unconventional oil production is from the Bakken (North Dakota, Montana), Eagle Ford (Texas) and the Niobrara (Wyoming and Colorado) shale formations (US Energy Information Administration, 2014a).

In 2012 the USA produced 8.9 million barrels of oil per day (this includes crude oil, shale oil, oil sands and natural gas liquids), the third largest producer in the world, behind Russia and Saudi Arabia. However, the USA is the world leader in producing oil and natural gas from hydraulic fracturing with 1.6 million barrels per day extracted from tight oil formations in 2012. Projections suggest that hydraulic fracturing will produce 4.5 million barrels per day by 2035, accounting for most of the US increase in oil production (BP, 2013). The US is poised to become the largest producer of liquid fuels in the world, primarily due to tight oil growth (BP, 2014b).

In 2012 the USA was the world's largest producer of natural gas, producing 681 billion cubic meters (Bcm). US production of shale gas output is projected to rise from 255 Bcm yr^{-1} in 2012 (37 % of total production) to 672 Bcm yr^{-1} in 2035 (BP, 2014a). Shale gas was just 2 % of US natural gas production in 2004 but by 2035 it will be 63 %. However, these oil and natural gas projections are highly uncertain with the quantity of oil produced in 2040 differing by a factor of two under a scenario of high oil and gas resources vs. a scenario of low oil and gas resources (US Energy Information Administration, 2014b).

With the increase in unconventional oil and natural gas has come an increase in fugitive emissions of hydrocarbons to the atmosphere in quantities great enough to influence local and regional-scale ozone production (Katzenstein et al., 2003; Kemball-Cook et al., 2010; Edwards et al., 2014). This impact was revealed in an unexpected way during early 2008 when hourly average ozone mixing ratios exceeded 140 ppbv during February in the rural Upper Green River Basin, of Wyoming (Schnell et al., 2009). In situ measurements revealed that the high wintertime ozone levels were due to a strong temperature inversion that trapped $\mathrm{NO_x}$ and hydrocarbon emissions from the natural gas industry. The trapping of the emissions was facilitated by high mountains on three sides of the basin. A key contributor to the ozone formation was deep snow cover which reinforced the temperature inversion, and also reflected UV radiation back through the inversion layer, essentially doubling the amount of available UV radiation necessary for ozone production. This phenomenon has also been observed in the Uintah Basin, Utah, impacted by both oil and natural gas extraction (Edwards et al., 2013, 2014). Multiple years of data from these two regions demonstrate that without deep snow cover, the high ozone values do not occur (Oltmans et al., 2014). Recent work in the UK context (Sommariva et al., 2014) has shown the range and difference in UK shale VOC profiles.

The impact of emissions from the oil and natural gas industry on ozone outside of these rural, mountain-ringed basins is less certain. For example, field studies have been carried out across the Denver–Julesburg Basin in north-eastern Colorado to quantify emissions from the oil and natural gas industry but accurate estimates for some gases are complicated by emissions from nearby urban areas (Pétron et al., 2012). However, relationships between particular VOCs can be used to clearly distinguish oil and natural gas emissions from urban emissions. VOC measurements from a site on the northern edge of the Denver metropolitan area were analysed to demonstrate that more than 50 % of the VOC-OH reactivity was attributable to emissions from oil and natural gas operations, indicating that these emissions are a significant source of ozone precursors (Gilman et al., 2013).

Several recent studies using chemical transport models suggest that emissions from the oil and natural gas industry can produce local and regional scale ozone enhancements (Kemball-Cook et al., 2010; Rodriguez et al., 2009; Carter and Seinfeld, 2012; Olaguer, 2012). The reliability of these modelling studies is limited by the emissions inventories which are difficult to accurately produce owing to the heterogeneity of sources: type of gases emitted from a shale play; number of active well heads; integrity of infrastructure; emissions associated with well-completion vs. well operation; usage of venting or flaring (Field et al., 2014). The most recent U.S. EPA estimates indicate that NO_x emissions from US petroleum and related industries only amounted to 5 % of total US anthropogenic NO_x emissions in 2013, but doubled between 2004 and 2013 (US Environmental Protection Agency, 2014). Likewise VOC emissions increased by a factor of four over the same period, accounting for 14 % of total US anthropogenic VOC emissions in 2013. However, these U.S. EPA estimates are highly uncertain. The U.S. EPA recently stated that it had not anticipated the tremendous nationwide growth in this sector and that it has limited directly-measured air emissions data from several important oil and gas production processes. The report recommends that the EPA produce a comprehensive strategy for improving air emissions estimates for oil and natural gas production (US Environmental Protection Agency, 2013). Until the emission inventories can be improved great uncertainty will surround model estimates of the impact of the oil and natural gas industry on ozone pollution.

One final consideration of the potential for the oil and gas industry to affect tropospheric ozone is through its impact on global methane levels. Methane leaks from the oil natural gas industry may be a contributing factor to the renewed increase in global methane concentrations (Nisbet et al., 2014). For example, hydraulic fracturing in Utah may locally leak 6 to 12 % of gas production to the air (Karion et al., 2013). Figure 37 shows data from a series of studies including satellite remote sensed data that all show significant methane leakage beyond official EPA estimates (Schneising et al., 2014; Kort et al., 2014). However, owing to the great uncertainty of many aspects of global methane emissions, especially from US unconventional oil and natural gas activities, much more research is required to understand the impact of unconventional oil and natural gas activities on global methane concentrations (Brandt et al., 2014).

4.10 Radical chemistry, radical changes

Radicals are central to the chemistry of the atmosphere; from the destruction of O_3 in the stratosphere, to the production and destruction of O_3 in the troposphere, radicals drive atmospheric composition change (Monks, 2005). The inorganic HO_x radicals (OH, HO_2) are regarded by many in the field of atmospheric chemistry as the most influential of all radicals, as such a great amount of effort has gone into understanding their impacts and fate in the atmosphere (Heard and Pilling, 2003; Monks, 2005; Stone et al., 2012).

Recent laboratory and modelling studies have shifted attention to improved understanding of the fate and role of organic radicals. The organic radicals of importance to atmospheric chemistry can be classified as organic peroxy radicals (RO_2) (Sect. 2.1.1), organic oxy radicals (RO) and the so called Criegee intermediates (CI), a class of biradical compounds believed to be formed mainly from the reaction of O_3 with alkenes.

In the following section we briefly review the main aspects of the chemistry of organic radicals and highlight the latest discoveries in their chemistry. Significant use of the review of Orlando and Tyndall (Orlando and Tyndall, 2012) is made and for further details we refer the reader to their work.

RO_2 are produced in the atmosphere by the OH (and NO_3) initiated oxidation of VOCs. Once formed RO_2 are lost via reactions with NO, HO_2 and other RO_2. Whilst reactions with halogens (X) and halogen oxides (XO) have been known about for several decades, their importance for inclusion in studies of tropospheric O_3 chemistry has traditionally been expected to be small (see Sect. 4.4 for more details). The $RO_2 + NO$ reaction is known to have two product channels. The first forming NO_2, hence propagating tropospheric O_3 formation; the second channel leads to the production of an organic nitrate ($RONO_2$) via a complex rearrangement, the exact mechanism of which is still uncertain (Dibble, 2008). We will not dwell on the chemistry of $RONO_2$ here, but suffice it to say these moieties allow O_3 precursors to be transported over great distances owing to their much longer atmospheric lifetime than NO_2. The kinetics of the $RO_2 + NO$ reaction limit the RO_2 lifetime to only a few seconds when $[NO] > 1$ ppbv (see Sect. 3.1 of Orlando and Tyndall, 2012 for references). Broadly speaking the $RO_2 + NO$ reaction can be classed as the most important of the RO_2 loss reactions to include for modelling O_3 production in the troposphere. The products of the reaction between RO_2 and HO_2 depend strongly on the structure of the RO_2 (Orlando and Tyndall, 2012). Traditionally the reaction between RO_2 and HO_2 has been thought of as a radical sink, hence limiting the propagation of $RO_2 + NO$ reactions and so reducing the potential O_3 production. The major product of this reaction for an alkyl RO_2 (R'RCHOO) is an organic hydroperoxide (ROOH), a compound that is predicted to be lost from the atmosphere via deposition or aqueous uptake faster than its photodissocation can reform precursor radicals. The kinetics of the self ($RO_2 + RO_2$) and cross reactions ($RO_2 + R'O_2$) of RO_2 (see Sect. 3.5 of Orlando and Tyndall, 2012 for references) limit the importance of these reactions to laboratory studies and parts of the atmosphere where concentrations of RO_2 are high (e.g. high BVOC emission regions).

For RO_2 to have a big impact on the composition and chemistry of the atmosphere they must propagate radical production. RO are produced almost exclusively as products of the reactions of RO_2 with NO. In general RO are very reactive and either undergo unimolecular decomposition (on the time scale of miliseconds) or react with O_2

producing HO_2 radicals (see Sect. 2.1.1). Archibald et al. (2007) used a box model to investigate the importance of the reaction:

$$RO + NO_2 + M \rightarrow RONO_2 + M \quad \text{(R13)}$$

and concluded that for CH_3O, Reaction (R13) could be a significant source of CH_3ONO_2 under the high NO_2 conditions found in many megacities, but that the unimolecular decomposition and reaction of O_2 with RO limits the importance of Reaction (R13) to CH_3O only.

Owing to very significant disagreement between model simulations and observations of HO_x radicals in pristine environments (Lelieveld et al., 2008; Whalley et al., 2011), a number of recent studies have focused on trying to better understand the role of NO_x free radical propagating chemistry for RO_2. In pristine environments the loss of RO_2 was traditionally thought to be dominated by the radical terminating reaction between RO_2 and HO_2. However, for acyl RO_2 (RC(O)OO) recent work has shown that the reaction of RO_2 with HO_2 has a major radical propagating product channel generating OH and RO_2 (see Sect. 3.4 of Orlando and Tyndall, 2012 for references). Based on this evidence Lelieveld et al. (2008) postulated that the reaction of RO_2 with X (where X reacted with a rate coefficient similar to that for $RO_2 + NO$) propagated radicals and was able to reconcile the model measurement disagreement for HO_x in the Amazon. However, Lelieveld et al. (2008) were unable to provide direct evidence for the structure of the unknown reaction partner, X. In much earlier modelling work, Frost et al. (1999) speculated that near-IR absorption by RO_2 could lead to intramolecular conversion and yield HO_x radicals. Whilst a great deal of work has been performed identifying the absorbance features of RO_2 in the near IR (e.g. Kline and Miller, 2014), to date there has been almost no laboratory evidence of HO_x formation following absorption by RO_2 in the near-IR. However, Maccarone et al. (2013) have recently shown that arylperoxy radicals (RO_2 derived from aromatic hydrocarbons) are able to photo-dissociate in the visible spectrum to yield $O(^3P)$, and hence produce O_3 in the troposphere, without the need for NO_x. As highlighted by the work of Lelieveld et al. (2008) and Frost et al. (1999), modelling experiments are increasingly being used to help direct laboratory studies in the search for radical propagating reactions. Archibald et al. (2009) investigated the possible reaction between RO_2 and OH using a simple box model of the marine boundary layer (MBL). In their study Archibald et al. (2009) suggested three different mechanisms for the $RO_2 + OH$ reaction yielding three unique product sets, two propagating radicals and the third leading to the formation of alcohols. The reaction they modelled was, at the time, very speculative and as such no kinetic studies had been performed. As such Archibald et al. (2009) used the kinetics of $RO_2 + X$ and $RO_2 + XO$ reactions as analogy. Their model calculations concluded that the $RO_2 + OH$ reaction would have little impact on HO_x under conditions encountered in the MBL. Recently Bossolasco et al. (2014) have measured the direct kinetics for the reaction between RO_2 and OH and have shown that it is extremely fast ($k \approx 2.8 \pm 1.4 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$), potentially twice as fast as the upper limit used by Archibald et al. (2009). The importance of this reaction under conditions similar to those found by Lelieveld et al. (2008) is yet to be explored.

Whilst unimolecular RO_2 isomerisations have been known about in combustion chemistry (where $T > 600\,\mathrm{K}$) for several decades (e.g. Hughes et al., 1992), the importance of this process for the loss of RO_2 in the troposphere was thought insignificant – until recently. The RO_2 isomerisation proceeds via internal H atom abstraction from the terminal oxygen of the –OO group to produce what in combustion chemistry is referred to as a QOOH (see Fig. 38). Using ab intio calculation, Peeters et al. (2009) and Da Silva et al. (2009) independently suggested a mechanism for RO_2 isomerisations in the oxidation of isoprene that they postulated could help improve the model-measurement mismatch reported by Lelieveld et al. (2008) for HO_x in pristine conditions. The focus on isoprene peroxy radicals has led to a number of new discoveries in the lab as well as from a theoretical point of view. Thanks, largely to developments in mass spectrometry and other analytical techniques, new products (isoprene epoxydiols – IEPOX; hydroperoxyaldehydes – HPALDS) have been elucidated, and their mechanisms and impacts on reconciling the "HO_x problem" tested (Crounse et al., 2011; Paulot et al., 2009).

In their work on updates to the chemical mechanism of isoprene oxidation, Archibald et al. (2010) reviewed several of the proposed mechanisms and concluded that whilst the isomerization reactions proposed by Peeters et al. (2009) had the most promise in reconciling the model-measurement disagreement, the reported parameters could not be fully reconciled with atmospheric observations of other species and existing laboratory data without some degree of parameter refinement and optimization, which would probably include a reduction in the peroxy radical isomerisation rates and a consequent reduction in the OH enhancement. Indeed, Crounse et al. (2011) provided the first laboratory evidence for the RO_2 isomerisations in the isoprene system but derived rate coefficients for the processes that where much smaller than those calculated by Peeters et al. (2009). However, modelling studies using the kinetics derived from their study suggested that 10–20 % of isoprene RO_2 would undergo unimolecular isomeriations (Crounse et al., 2011) and as such this is an important process to include.

An astonishing amount has been learnt about the atmospheric chemistry of the Criegee Intermediates (CI) over the last few years. Pioneering work carried out at the Advanced Light Source (Taatjes et al., 2008) provided the first detection and subsequent direct measurements of the kinetics of the CI (Welz et al., 2012). Traditionally CI have been thought to have been formed exclusively from the ozonolysis reaction of alkenes (as originally proposed by Criegee, 1948). However, the recent laboratory studies on small CI have utilized novel chemical routes, which avoid the reaction with O_3. For example, a large number of groups have used CH_2I_2 as a reagent for the formation of CH_2OO (via photolysis and reaction with O_2). It should be noted that CH_2I_2 one of the major iodine containing VOCs emitted in the marine boundary layer (Saiz-Lopez et al., 2011) and may be a direct source of CI in this environment. McCarthy et al. (2013) have shown that CH_2OO can also be produced via passing a mixture of CH_4 and O_2 through an electric discharge (through what remains an as yet unknown mechanism). Based on this evidence McCarthy et al. (2013) have postulated that it is likely that CH_2OO can be formed in the upper and free troposphere, given the large mixing ratios of CH_4 and O_2 in the upper troposphere and the relatively high density of electrical discharge (in the form of lightning flashes). Given that many of the reactions between O_3 and alkenes have small rate coefficients ($\sim 10^{-17}\,\mathrm{cm^3\,s^{-1}}$) it is important that these non-ozonolysis routes to CI production be quantified using model studies in order to better understand the burden of CI in the troposphere.

Of fundamental importance to understanding the chemistry of CIs is knowledge of their physical properties. McCarthy et al. (2013) have used a combination of methods to determine the geometry of CH_2OO, in good agreement with the work of Su et al. (2014). As well as now having great insight into the geometry of CH_2OO, a number of studies have shed light on the absorption spectrum of CH_2OO in the UV/vis (e.g. Beames et al., 2012; Sheps, 2013) Beames et al. (2012) and Sheps (2013) have shown that there is strong absorption by CH_2OO in the 320–400 nm range. Whilst this may have implications for additional loss of CH_2OO by photolysis, the large cross section in this region has the benefit of making cavity ringdown spectroscopy laboratory studies of the kinetics of CH_2OO (and other CIs) possible – opening up a number of avenues for greater understanding of these ephemeral but crucial intermediates in the oxidation of VOCs in the atmosphere.

What seems to be emerging from the plethora of laboratory studies on the kinetics of CI reactions is that they react very fast! For example, Su et al. (2014) have shown that the bimolecular self-reaction of CH_2OO has a rate constant near the gas kinetic limit ($k = 4 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$). Su et al. (2014) determined that the reaction proceeds via a CH_2OO dimer – where the zwitterionic character of the CH_2OO allows for barrierless addition of the terminal O atoms with the central C atom. This dimer is predicted to dissociate to produce two CH_2O (formaldehyde) and O_2 in it's excited electronic state ($O_2(^1\Sigma_g)$). Such a fast self-reaction has implications for the analysis of previous laboratory studies in this system. Similarly fast kinetics have been observed for CIs reacting with organic acids. Using a combination of time resolved laboratory experiments, Welz et al. (2014) have very recently shown that the reactions of the C1 and C2 CIs with HCOOH and CH_3COOH are several orders of magnitude faster than previously inferred from alkene ozonolysis reactions ($k \sim 1.0 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$). Although products of the reaction were not detected, it is likely that highly condensable products will form, potentially contributing to SOA formation and growth. Although it is interesting to note that the CI seem more reactive than RO_2 with a number of compounds, it is paramount to understand the dominant loss processes of the CI in order to understand their abundance. Before many of these direct kinetic experiments were performed it was widely assumed that in the troposphere the reaction with H_2O would dominate over other loss reactions, in spite of slow (although uncertain) kinetics. Welz et al. (2012) reported an upper limit for the $CH_2OO + H_2O$ reaction rate coefficient ($k = 4 \times 10^{-15}\,\mathrm{cm^3\,s^{-1}}$). Relative rate experiments have yielded a number of other estimates of the rate coefficient for this. Ouyang et al. (2013), who studied the reaction of NO_2 with CH_2OO, estimated $k = 2.5 \times 10^{-17}\,\mathrm{cm^3\,s^{-1}}$. In their study, Ouyang et al. (2013) were able to show that the reaction produces NO_3 – the most important oxidant at night. So far inclusion of this reaction into modelling studies has not been performed and estimates of the importance of this process for night-time chemistry are needed. Based on detection of HCHO, Stone et al. (2014) were able to put an upper limit on the reaction of the CI with H_2O of $k = 9 \times 10^{-17}\,\mathrm{cm^3\,s^{-1}}$, significantly smaller than the estimates for this reaction by Welz et al. (2012). They suggested that this much lower reactivity may mean that previous conclusions from modelling studies where H_2O was calculated as the dominant loss process may need to be revised. Combining the results of Welz et al. (2014) and Stone et al. (2014) we speculate that it is possible that in many environments where organic acids are present at the ppb level, reaction with these acids may be the dominant loss process for CI. Interestingly, Taatjes et al. (2013) have shown that the anti-$CH_3CHOOCI$ reacts with H_2O very fast ($k = 1.0 \times 10^{-14}\,\mathrm{cm^3\,s^{-1}}$), suggesting that the lack of reaction between CH_2OO and H_2O may not be representative of all CI.

5 Policy context

Within the policy context, much of the focus on ozone has been on ozone as an air pollutant (e.g. OECD, 2012; EEA, 2007, 2009, 2011; Royal Society, 2008; Fowler et al., 2013a). As recently stated the aim of much policy with respect to ozone and air quality is “to achieve levels of air quality that do not result in unacceptable impacts on, and risks to, human health and the environment” (Fowler et al., 2013a) (see also Sect. 3) within some measure of reasonable cost. This process requires an understanding of the messages from research and monitoring activities to develop new insights. Policy, to date, requires methods of assessing compliance to metrics that quantify impact. Owing to the transboundary nature of ozone, much focus has been on regional and hemispheric impact of metrics and mitigation.

Throughout this section certain metrics will be detailed, the main two of which are AOT40, the seasonal accumulated exposure above 40 ppb (80 $\mu g\,m^{-3}$) during daylight hours, this is normally expressed as a cumulative exposure (ppb h or ppm h) and SOMO35 the sum of the amounts by which maximum daily 8 h concentrations of ozone (in $\mu g\,m^{-3}$) exceed 70 $\mu g\,m^{-3}$ (35 ppb) on each day in a calendar year.

5.1 Policy metrics for ozone

Ozone is a powerful oxidant which can cause adverse effects on human health, and vegetation. As a result, air quality standards for ozone have been established to mitigate these effects. Ozone can also damage some materials, particularly rubber and plastics, but no standards specifically address these effects. Ozone is a unique pollutant in that different areas of the ozone concentration frequency distribution are affected by different mechanisms and hence could require significantly different policy responses. The averaging times of different ozone metrics are also of crucial importance for policy (see e.g. Pappin and Hakami, 2013; Lefohn et al., 2010).

Health-related standards have up to now been expressed as one hour or eight-hour averages, the latter arising originally from chamber studies of human exposures where the maximum effects were observed over exposures of around eight hours. Such short term peak ozone concentrations based on averaging times of the order of hours, such as those observed in “smog” episodes, are formed from the well-known VOC/NO_x chemistry (see Sect. 2.1.1). These reactions occur typically over timescales of hours to a few days, in conditions of low wind speed and strong sunlight, and hence the spatial scale of such episodes and the policy response area, is of the order of 100, s to ~ 1000 km. Controls on precursor emissions across Europe are therefore required to mitigate these peaks within European nations. Figure 40 shows a comparison of a number of national and international ozone air quality standards.

Effects on vegetation however are more closely related to longer term exposures and in the recent EU Ambient Air Quality Directive (Directive 2008/50/EC) for example, the Target Value (see below) for the protection of vegetation is expressed in terms of AOT40 as an average from May to July (defined in more detail later). This longer exposure period and averaging time, with a threshold close to the tropospheric baseline ozone level means that emission controls would be required over a much wider area than those to mitigate the health-related one/eight hour average concentrations discussed above, and could also involve other, more long-lived precursors such as methane.

There are several levels of "standard" in use, with differing legal status. For example, the fundamental health effect evidence is used to inform the setting of WHO Air Quality Guidelines, below which the pollutant in question will not have adverse effects on public health. The Guidelines are set without regard to the technological, economic or social issues which might affect their achievability. In setting legally based standards however, some flexibility is often introduced to allow for difficulties of achieving the levels and/or to allow for year-to-year meteorological variability. For short-term standards this usually takes the form of allowing a number of exceedences of a given concentration over a year, and/or averaging over several years as in the case of the USA. Some standards in place around the world are shown in Table 3.

Although in some cases the "headline" concentration value in different countries' standards may be similar, the number of allowed exceedences of short term levels is crucially important in determining their relative stringency. These criteria are shown on the footnote to the Table 3. Moreover, the status of the standards is also very important. In the USA, the National Ambient Air Quality Standard (NAAQS) for ozone has the same mandatory legal status as those for the other criteria pollutants. In the EU however this is not the case as it was recognised that no single Member State could control the ozone levels measured within its territory because of the transboundary nature of ozone formation during "smog" episodes (Royal Society, 2008). In the EU Directives therefore, the ozone standard is a Target Value as opposed to a mandatory Limit Value in the case of the other pollutants. A Limit Value is 'to be attained within a given period and not to be exceeded once attained'. Target Values in contrast, are "to be attained *where possible* over a given period." The mandatory aspects of ozone control in the EU are contained within the National Emission Ceilings Directive which sets mandatory emission ceilings for individual Member States for NO_x and VOCs, which are designed, inter alia, to achieve reductions in ozone levels.

There are also standards in place to protect against damage to vegetation. In the EU Directive there is a Target Value of 18 000 $\mu g\,m^{-3}\,h$ for AOT40, defined as the sum of the difference between observed hourly concentrations greater than 80 $\mu g\,m^{-3}$ (≈ 40 parts per billion) and 80 $\mu g\,m^{-3}$ over a given period using only the one-hour values measured between 08:00 and 20:00 Central European Time (CET) each day. In the US the 8-hourly NAAQS in Table 3 is also designed to protect against damage to vegetation, so the spatial scale of policy responses to protect against vegetation damage in the EU and the USA are potentially quite different.

Two recent developments have important implications for policy responses for mitigating ozone concentrations. First, the work of the CLRTAP (Convention on Long-range Transport of Atmospheric Pollutants) Task Force on Hemispheric Transport of Air Pollution has shown that intercontinental transport of ozone and its precursors can make significant contributions to the exceedance of air quality standards and can even cause exceedances in their own right (HTAP, 2010). This has already led to challenges to air quality standard enforcement in California (Hand, 2014). In the case of Europe this suggests that emission reduction strategies should take into account measures and policies in North America. Likewise, plans to reduce ozone in North America should take into account emissions in Asia.

The second development relates directly to potentially new metrics to protect human health from adverse effects of ozone and the existence or otherwise of a no-effect threshold. The recent review of the health effect literature by WHO (WHO, 2013) has concluded that there is now evidence showing associations between long term (summer mean) ozone concentrations and respiratory mortality, and weaker associations with cardiorespiratory mortality. WHO recognised the uncertainties in this area but nonetheless suggested that long-term average WHO Guidelines and a long-term (possibly a summer mean) Target Value should be considered by the European Commission.

In parallel with these conclusions, the REVIHAAP report (WHO, 2013) also noted that evidence for a no-effect threshold for short-term impacts was inconclusive but recommended that SOMO10 as well as SOMO35 should be used in health impact assessments. These findings are significant for future policy on ozone. Long-term (summer) averages, as noted earlier, are partly determined by hemispheric or global emissions; to attain a threshold of 10 ppb hourly average in SOMO10 would also imply reductions of emissions on a global scale. If the evidence behind these emerging conclusions strengthens then the geographical scale of ozone reductions strategies will need to be extended beyond the regional level to hemispheric or global scales (Hsu et al., 2013).

5.2 Ozone mitigation and baseline ozone

Observational evidence suggests that baseline ozone concentrations as they effect Europe have been rising up until about 2000 (Wilson et al., 2012; Parrish et al., 2009; Simmonds et al., 2004; Jenkin, 2008; Derwent et al., 2006), though currently they appear to be falling (Logan et al., 2012; Parrish et al., 2012). An increasing background contribution to European ozone levels could represent a substantial future challenge to the attainment of ozone limit values (Derwent et al., 2010). With an increasing background contribution there is a requirement to control more ozone of anthropogenic European origin to achieve the limit. Models have shown (Derwent et al., 2010; Szopa et al., 2006) that the benefit to European emission controls can be significantly counterbalanced by increasing background ozone. These results were confirmed for a long-term perspective (2050) in Colette et al. (2013) that emphasized that air quality legislation was indeed anticipated to bear its fruit in reducing ozone exposure in the future, even if under business as usual scenario such as the RCP8.5, climate change and long range transport constituted a heavy penalty.

Similarly, in the US context there has been much debate as to the contribution and quantification of background ozone and its effect on the attainment of standards (Lefohn et al., 2014; Fiore et al., 2014). Lefohn et al. (2014) have explored the concept of an emissions-influenced background in an attempt on a continental scale to partition the controllable ozone (see Fig. 41). Fiore et al. (2014) noted that the largest model differences in the calculation of North American Background ozone, in this case a model construct, were linked to differences in contributions from the stratosphere, wildfires, lightning and isoprene chemistry.

The recent results of the 2013 revision (Amann et al., 2013) of the European Thematic Strategy on Air Pollution indicate that the reduction of 10 % of the 25 000 anticipated death attributed to ozone ambitioned by the 2005 TSAP should be safely achieved in 2025 with about 18 000 annual premature death under the scenario currently planned.

Fowler et al. (2013a), in their recent report on research findings in support of the EU air quality policy argued that “more attention needs to be given to treating ozone as a hemispheric transboundary issue” (see Sect. 5.3).

5.3 Hemispheric transport of ozone and it precursors in the policy context

Substantial efforts have been undertaken to quantify the importance of long-range transport of ozone from distant source regions as part of UNECE HTAP (2010). More than 20 global models conducted idealised source-receptor experiments to quantify hemispheric transport of ozone and its precursors and the key findings are reported in Fiore et al. (2009) and HTAP (2010). 20 % reductions in anthropogenic precursor emissions from North American, East Asian and South Asian sources reduce annual mean EU O_3 by about 0.4, 0.2 and 0.1 ppbV, respectively (HTAP, 2010). The influence of LRT has a seasonality, with the largest impact in spring (March–April: ~ 0.8 ppbV) and minimum impact in late summer (July–September: ~ 0.45 ppbV) (HTAP, 2010). This influence may appear small, but the equivalent O_3 response to a 20 % emission change over Europe itself is 1.5–2.0 ppbV in summertime, and is close to zero on a regional mean basis in winter when titration is important. It is worth noting that the HTAP emission reductions (20 %) have been exceeded in reality over Europe for the 1990–2009 period (EEA, 2011). By scaling the 20 % emission changes to the actual regional emission changes and accounting for the nonlinearity in ozone responses, (Wild et al., 2012) derived the ozone trend over Europe from 1960–2000 along with the contributions from the EU, external sources (i.e. LRT) and changing atmospheric CH_4. An increase of about 6.5 ppbV is calculated between 1960 and 1990, and a slight decrease from 1990–2000. More than half of the 1960–1990 trend came from non-European sources (2.1 ppb) and CH_4 (1.6 ppb), with only 2.8 ppb from changes in EU emissions.

A number of studies have focussed on the contribution of increasing precursor emissions over Asia to ozone over North America. Reidmiller et al. (2009) have used the HTAP simulations to demonstrate that precursor emissions from both East Asia and Europe influence the policy-relevant maximum 8 h average (MDA8) ozone metric, but note that regional emission controls over North America are 2–10 times as effective at reducing this ozone metric as the equivalent controls in these foreign regions. However, Lin et al. (2012), demonstrate that Asian emissions may contribute as much as 8–15 ppb ozone to MDA8 in the south-western US in springtime on days when ozone exceeds 60 ppb, indicating the important role that long-range transport may play in ozone exceedences. More recent work by Lin et al. (2014a) has shown that transport of the export-related Chinese pollution contributed 0.5–1.5 % of ozone over the western United States in 2006. This Chinese pollution also resulted in one extra day or more of noncompliance with the US ozone standard in 2006 over the Los Angeles area and many regions in the eastern United States. Equivalent studies focussing on air quality metrics in Europe have yet to be performed, but are likely to show smaller impacts given the greater transport distances from regions showing substantial emission increases.

5.4 Impacts of climate change

Jacob and Winner (2009) have undertaken a comprehensive review of the impact of climate change on air quality, including ozone. Despite regional differences, the dominating signal is one towards an increase of ozone levels induced by global warming (Stevenson et al., 2006), that led Wu et al. (2008) to coin the term “climate penalty”. The possible pathways for such a penalty include increasing continental temperatures, changing atmospheric humidity and changes in the prevalence of stable, anticyclonic conditions trapping pollutants in the boundary layer and possibly leading to higher surface ozone even without changes in anthropogenic precursor emissions. These meteorological factors may be supplemented by climate-driven changes in biogenic emissions of isoprene and in dry deposition of ozone. It is worth noting that in the lower free troposphere and in remote surface regions ozone is expected to decrease owing to increased water vapour in a warmer world (Jacob and Winner, 2009).

Bloomer et al. (2009) estimated the magnitude of these effects from surface ozone observations over the US at about 2.2 ppb $^{\circ}C^{-1}$. These effects have been quantified over Europe in several model studies (Colette et al., 2013; Meleux et al., 2007; Langner et al., 2012a, b; Andersson and Engardt, 2010; Manders et al., 2012; Hedegaard et al., 2008, 2013b; Katragkou et al., 2011). The general order of magnitude of the climate penalty over Europe is a few ppb by the middle of the century. Langner et al. (2012b) point out a larger increase at the 95th percentile of hourly ozone, suggesting that the effects of climate change may be particularly important during high ozone events. The effects of changes in isoprene emissions and dry deposition have been quantified separately by Andersson and Engardt (2010) who find increases in mean ozone of up to 5 ppb by 2050 in some parts of western Europe, with as much as 60 % of this change attributed to decreased dry deposition, and with increased isoprene emissions contributing up to 1 ppb. As noted above large uncertainties remain regarding the impact of climate change on biogenic emissions, with up to a factor five difference in isoprene change reported in a multi-model ensemble (Langner et al., 2012b).

There are few studies that proposed quantitative comparisons of the relative impact of climate change and air pollution mitigation strategies on surface ozone. Existing investigations all agree on a larger impact of air quality policies (Tagaris et al., 2007; Hedegaard et al., 2013; Colette et al., 2013), endorsing to the efficiency of currently planned mitigation strategies, despite external penalties brought about by climate change and long range transport.

It should be noted however that studies focusing on the iimpacts of climate change use long-term projections (typically 2050) which have substantive precursor mitigation. Given the magnitude of the response to precursors changes, the sensitivity to the choice of the scenario is worth noting (Fiore et al., 2012). Pioneering studies relied on projections originally designed for climate projections (SRES, Nakicenovic et al., 2000 or RCPs, van Vuuren et al., 2011), but the ozone precursor information in such scenarios was solely provided to assess radiative forcing and their use for surface air quality projections constitutes a deviation from their original purpose. The use of emission projections relying on policy relevant emissions factors such as the Global Energy Assessment (Riahi et al., 2012), the ECLIPSE (Klimont et al., 2013a, b) or PEGASOS datasets are more reliable.

While the implications of these effects for surface ozone and air quality policy are substantial, there is still considerable uncertainty in the magnitude of these indirect climate effects, and improved understanding of the processes controlling these atmosphere–land surface interactions is needed.

6 The future – air quality and climate

Recently, pollutants that typically fall under the “air quality” categorization have been receiving increasing attention for their role in climate change and their impact on radiative forcing. More specifically, significant focus has been on ozone, methane (as a GHG and an ozone precursor), and aerosol constituents (mostly the black carbon (BC) component). Significant potential exists for co-benefits with coordinated air quality and climate policies. A number of reviews have recently addressed various aspects of the linkages between air quality and climate, from the chemistry interactions to the policy implications (von Schneidemesser and Monks, 2013; Isaksen et al., 2009; Fiore et al., 2012; Unger, 2012). For more details, see these reviews. Here, a brief overview of the topic will be given, with a focus on ozone and the latest developments.

In addition to being an air pollutant with significant adverse health effects, ozone is also a greenhouse gas. A recent estimate of ozone's radiative forcing effect (from pre-industrial times to the present day) is $+0.40\,\mathrm{W\,m^{-2}}$ (Myhre et al., 2013), other estimates include +0.44 and +0.23 (Unger, 2012; Fiore et al., 2012). For comparison, the RFs attributed to methane and CO_2 are $+0.48\,\mathrm{W\,m^{-2}}$ and $+1.66\,\mathrm{W\,m^{-2}}$, respectively (IPCC, 2007). The ozone precursors NO_x, NMVOCs, and CO, have little to no direct effect on climate, but influence climate and radiative forcing through their effects on ozone and methane, as well as atmospheric oxidant concentrations and indirect ecosystem effects (von Schneidemesser and Monks, 2013 and references therein). Reductions in NMVOCs and CO tend to be synergistic and result in overall decreases in RF, although the effects can be fairly minor, especially for NMVOCs (Collins et al., 2013). The effect of NO_x on climate/radiative forcing is much less straightforward. A variety of interactions, feedbacks, and ecosystem effects confound the picture for NO_x, resulting in significant uncertainty and often times competing effects on climate. A variety of modelling studies have evaluated the various direct and indirect effects (Collins et al., 2010, 2013; Shindell et al., 2009; Fry et al., 2012; Colette et al., 2011) and a summary can be found in von Schneidemesser and Monks (von Schneidemesser and Monks, 2013). More research is needed on this topic.

Methane, an important greenhouse gas in its own right, is also an ozone precursor. With a lifetime of approximately a decade in the atmosphere, methane is well-mixed globally and therefore has a significant influence on background ozone levels. Methane is a distinct win-win possibility for air quality and climate in that reductions in methane emissions would decrease ozone, including baseline ozone, and thereby lessen adverse impacts on vegetation and human health, but also benefit climate by reducing two GHGs simultaneously (Fry et al., 2012; Shindell et al., 2012; Isaksen et al., 2014). A model study investigated the air quality (O_3) and climate benefits of methane reductions and found that O_3 reductions were relatively linear with respect to reductions in methane emissions. In addition, the CH_4 emission reductions did not depend strongly on location, as the climate and air quality benefits were realized globally, which would allow for the most cost effective emission controls to be implemented (Fiore et al., 2008).

However, the interactions go both ways. Not only does ozone affect the climate, but changes owing to climate change will also influence ozone production. This effect is known as the “climate penalty”. A variety of effects resulting from a changing climate will potentially influence ozone concentrations, some increasing ozone, some decreasing ozone (Rasmussen et al., 2013). Many of these effects are associated with a significant amount of uncertainty. Climate changed induced increases in methane emissions from wetlands, stratosphere–troposphere exchange of ozone, lightning NO_x, and regional stagnation all consistently lead to increased ozone when investigated, while increases in dry deposition and humidity consistently lead to decreases in ozone (Fiore et al., 2012; Isaksen et al., 2009). Other climate change induced effects such as increased wildfires have a much more uncertain effect on ozone. For example, for a regional study in California, climate-related perturbations (temperature, biogenics and water vapour) led to combined peak 1 h ozone increases of up to 11 ppb (Millstein and Harley, 2009).

In a model ensemble study by Colette et al. (2012) future (2030) air quality in Europe owing to just air quality policy or air quality and climate policy was compared. The base case included all current and planned air quality measures up to 2030 and was compared to a “sustainable” case with the air quality as well as climate measures (2° target and energy efficiency improvements). Depending on the scenario annual mean O_3 was found to slightly increase over NO_x saturated areas but the overall O_3 burden would decrease substantially, including exposure to detrimental levels of O_3 for health

(Kinney, 2008). The air pollution measures were responsible for the main improvements in ozone, but an additional co-benefit of at least 40 % (depending on the indicator) was attributed to the climate policy (2012). A study by Crawford-Brown et al. (2012) focused on the co-benefits to O_3- and PM-related health effects resulting from implementation of climate policy in Mexico. A base case scenario was compared to a decarbonisation scenario where CO_2 emissions in Mexico would be reduced by 77 % by 2050. The co-benefits to air quality were reductions in O_3 of 11–13 % by 2050. The reduction in non-fatal diseases from O_3 and PM related health co-benefits was valued at USD 0.6 billion year^{-1} (Crawford-Brown et al., 2012). Both of these studies show that there are significant benefits to pursuing coordinated policies for air quality and climate, and not only for the improvement of O_3 related air quality. Rypdal et al. (2005) have commented on the challenges for putting tropospheric ozone in climate agreements.

7 Conclusions

Ozone remains central to atmospheric chemistry as the initiator, propagator and product of photochemistry. Its influence is felt on human health, ecosystems and climate. Ozone though ubiquitous remains an enigma. In many places in the Northern Hemisphere mid-latitudes ozone in some senses remains a paradox, the high summertime peak levels decreasing but the regional background levels rising (Fishman et al., 2014; Parrish et al., 2012). Globally this points to the need to treat ozone across the range of scales, a transboundary issue, but with an emphasis on the hemispheric scales (Fowler et al., 2013a; Simpson et al., 2014). Recent air pollution episodes in Europe have pointed to the continuing need to think about the how climate change policies interact with air quality policy and what can be learnt from current episodes (Monks, 2014). There remain a number of clear challenges for ozone such as explaining surface trends, incorporating new chemical understanding, ozone-climate coupling as well as a better assessment of impacts.

With respect to the future, studying the atmospheric chemistry of ozone relies on the continuing interplay of laboratory studies of fundamental parameters being integrated with our best theories using numerical models and evaluated against in situ observations. This “three-legged” stool approach is generic, but is a vital model to use to understand not only ozone but the wider chemistry in the atmosphere (Abbatt et al., 2014).

One area implicit in this review, which hasn’t been discussed explicitly, has been the role of observations in understanding, quantifying and describing ozone across the scales. Observations of ozone and its precursors underpin and drive the development of our knowledge base (Laj et al., 2009). Bowman has argued that the global nature of pollution and climate change requires a new observing system for ozone (Bowman, 2013). A key feature of the system should be the ability to predict and attribute ozone to emissions. A combination of satellites, ground-based remote sensing and ground-based observations are needed with geostationary observations (Lahoz et al., 2011) being an observational anchor (see Fig. 42).

It is clear that space observations offer the global view and repeatability not easily available from other observing systems. Measurement of ground-level ozone from space still remains a significant challenge (Foret et al., 2014; Duncan et al., 2014). There is future potential for global observations of tropospheric ozone from space either directly (Sellitto et al., 2013) or through a combination with models (Zoogman et al., 2014; Martin, 2008). Duncan et al. (2014) have recently reviewed the application of satellite data to air quality applications including common mistakes to avoid.

The growth of small sensors for a range of trace species including ozone has the potential to offer insights on unheralded spatial and temporal timescales (Snyder et al., 2013; Mead et al., 2013; Piedrahita et al., 2014). As illustrated in Fig. 43, there are potential new avenues opened up for air quality monitoring by the deployment of extensive networks of these sensors. The absolute measurement of ozone remains a challenge with these sensors owing to interferences (Mead et al., 2013). New developments suggest these configurations of sensor technologies can give long-term atmospheric performance for the measurements of ozone (Williams et al., 2013; Bart et al., 2014).

There may yet be new links and biospheric feedbacks driven by ozone to be explored. For example, the effect of elevated O_3 and whitefly herbivory significantly increased tomato volatiles, which attracted *E. Formosa* wasps and reduced the whitefly feeding on tomatoes (Cui et al., 2014).

There are interesting attempts to make public outreach on the effects of ozone on plants and crops. Fishman et al., have described a establishment of an “Ozone Garden” (Fishman et al., 2014). The garden provides real-time measurements of O_3 concentrations as well as firsthand observations of the detrimental effects of this pollutant. Meteorological data, as well as the O_3 concentrations from the monitor, are recorded and publicly disseminated in near-real time via the internet.

Looking forward it is clear that levels and patterns of global ozone will continue to change, impacting global warming, air quality, global food production and ecosystem function. There remains a need for continuing research to quantify impacts and interactions across all the scales. The issues around tropospheric ozone are not “solved” (Guerreiro et al., 2014) and new data continues to shed light on more aspects of ozone and its interactions in the global atmosphere.

Acknowledgements. This review was prepared as part of the European Commission project ACCENT Plus (grant agreement 265119).

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Table 1. Selected estimates of the non-stomatal resistance for ozone to snow, water, soil and plant surfaces from measurements.

Reference	Type	Surface	R_{ns}, s m^{-1}
Chang et al. (2002)	chamber	Agricultural soil (no data on moisture content)	ca 625 ca 475
Wesely et al. (1981)	Field µmet	Wet bare soil Snow −11 °C −5 °C −1 to 2 °C Lake water	1000 ± 100 (370–2100) 2000 ± 200 3500 ± 200 3300 ± 300 9000 ± 300
Sanchez et al. (1997)	Field µmet	Semi-arid steppe (wet and dry)	Dry 275 Wet 437
Rondon et al. (1993)	Field chambers	Coniferous trees	200–330
Granat and Richter (1995)	Field chambers	Pine	500–2500
Coe et al. (1995)	Field µmet	Sitka spruce	ca 133
Fowler et al. (2001)	Field µmet	Dry moorland	200–400
Grantz et al. (1995)	Field µmet	Wet and dry grape	Dry 1020 Wet 292[a]
Grantz et al. (1997)	Field µmet	Wet and dry cotton	Dry 770 Wet 3030
Zhang et al. (2002)[b]	Field µmet	Wet and dry: Mixed forest Deciduous forest Corn Soybean Pasture	244–970 397–1831 308–1332 137–735 571–879
Gerosa et al. (2005, 2009)	Field µmet	Mediterranean Oak (Quercus ilex)	Dry 249 Wet 177 Avg 67–204
McKay et al. (1992) and references therein	Laboratory chambers and field	Sea water & saline solutions	650–6600
Gallagher et al. (2001)	Field µmet	Coastal waters	950 ± 70
Coyle et al. (2009)	Field µmet	Potatoes Wet canopy Dry canopy	276
Neirynck et al. (2012)	Field µmet	Temperate Forest	136

[a] From data reported in Grantz et al. (1997).

[b] Data derived from references therein.

Table 2. Reported mean O_3 for megacities.

Location	Mean O_3 (ppbv)*	Statistic/year	Ref
Beijing, China	31	6 site average, 2001–2006, JJAS	Tang et al. (2009)
Bangkok, Thailand	17	Annual average, 1 h, 1995–2008	Zhu et al. (2012)
Cairo, Egypt	46	Dec 2004–Nov 2005	Khoder (2009)
Delhi, India	24	1997–2004, annual avg	Ghude et al. (2008)
London, UK	19 (38 $\mu g\,m^{-3}$)	Annual average hourly data; suburban site (Eltham) 2009	http://uk-air.defra.gov.uk
Los Angeles, CA, USA	122	2005–2007, national 8 h ozone design values (daily 8 h max from running avgs)	Cox et al. (2009) (accessed 8 Aug 2013)
Mexico City, Mexico	93	City plume, avg from flight measurements, MIRAGE-MEX campaign	(Tie et al., 2009)
Tehran, Iran	34 (68.84 $\mu g\,m^{-3}$)	2010, annual 8 h avg	Naddafi et al. (2012)

[*] Concentrations originally reported in $\mu g\,m^{-3}$ were converted to ppbv using the simple conversion of 1 ppb = 2.0 $\mu g\,m^{-3}$, assuming 1 atm pressure and 25 °C.

Table 3. Comparison of world standards for ozone.

Country/region	Ozone level (ppb)	Averaging time	Nature of level
WHO	50	Daily max. 8 h mean	Guideline[1]
EU	60	8 h running	Target value[2]
	60	Average	Long Term Objective
USA	75	8 h	National standard[3] primary and secondary
California	90	8 h	State standard not to be exceeded
	70	1 h	
UK	50	8 h	Objective[4]
Canada	63	8 h	2015
	62	8 h	2020 Both "voluntary guidelines"
Mexico	80	8 h	5th maximum taken over 1 year
	110	1 h	
China	80	1 h	Grade I
	100	1 h	Grades II and III Liu et al. (2013b)
India	50	8 h	
	90	1 h	

[1] WHO also quotes 120 ppb daily max. 8 h mean as having "significant health effects" and gives 80 ppb daily max. 8 h mean as an interim target.

[2] EU value not to be exceeded on more than 25 days per calendar year averaged over 3 years.

[3] USA value – the 3 year average of the fourth-highest daily maximum 8 h average measured at each monitor in an area must not exceed 160 µg m^{-3}/0.075 ppm.

[4] UK Objective maximum 8 h running mean in a day, not to be exceeded more than 10 times per year.

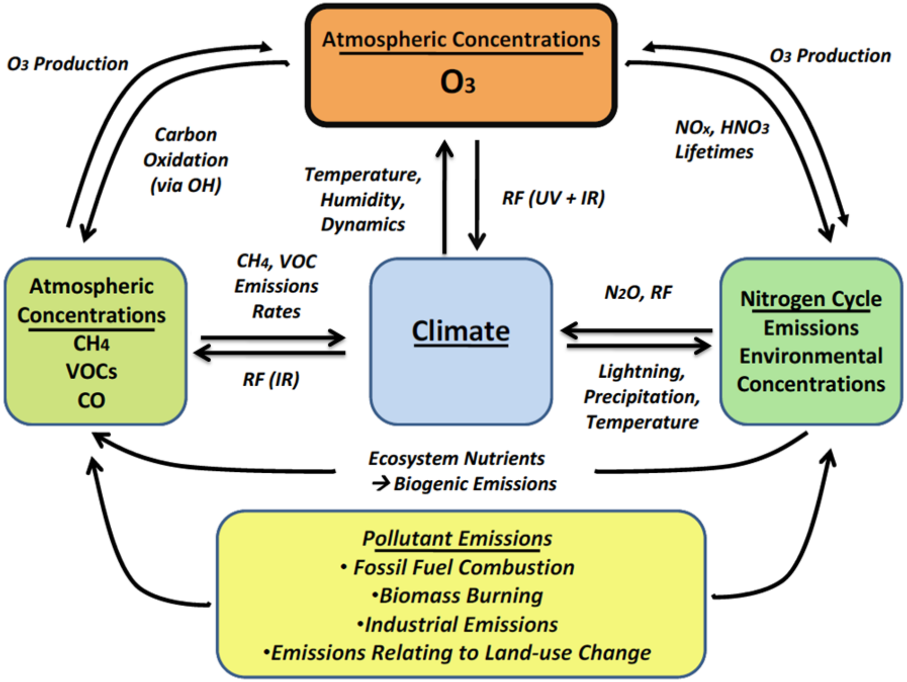

Figure 1. Schematic representation of the interactions of ozone in the earth system (EPA, 2009).

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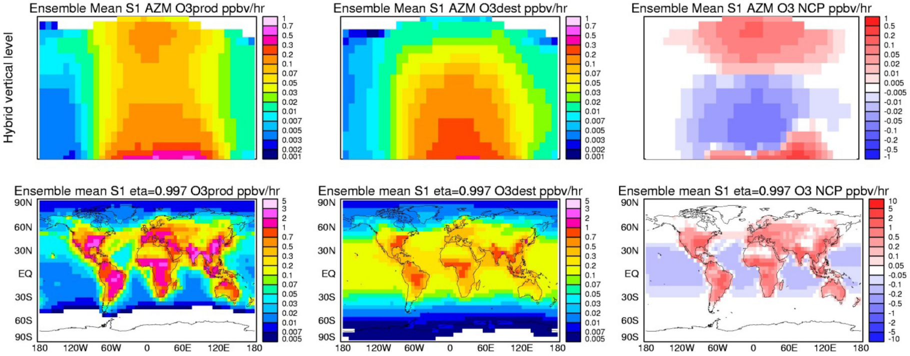

Figure 2. Multi-model mean (20 models) year 2000 ozone budgets (units: ppb h^{-1}). Top row: annual zonal mean (AZM) chemical production; chemical destruction; net chemical production. Vertical scale is from surface to approximately 100 hPa. Bottom row: maps of same quantities in the surface model layer (Stevenson et al., 2006).

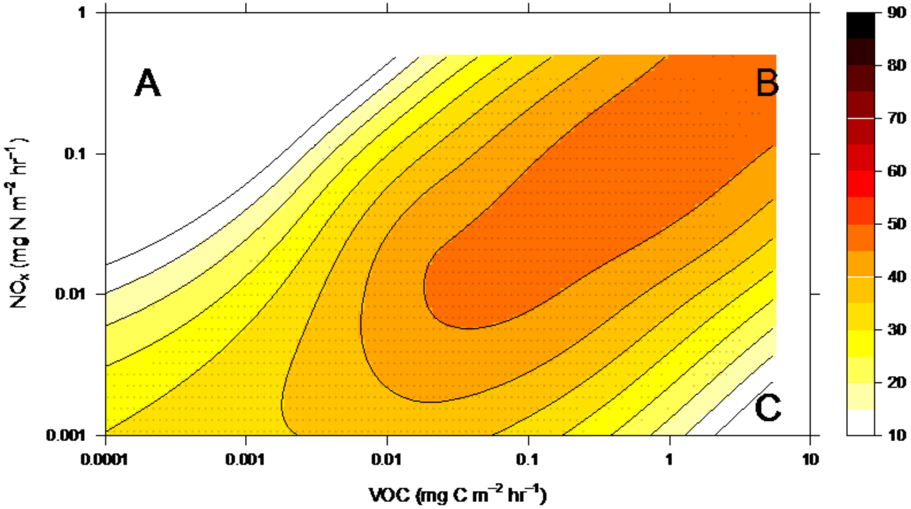

Figure 3. O_3 mixing ratios (ppb) as a function of VOC and NO_x emissions as computed using the UKCA model of atmospheric chemistry (Archibald et al., 2011). Three main regions are identified. Top left corner: region of NO_x saturation and O_3 titration. Bottom right corner: region of VOC saturation and O_3 destruction. Diagonal elements: efficient conversion of NO-NO_2 and hence O_3 production increasing with increasing VOC and NO_x emissions (NB $\log_{10}$ scales for emissions).

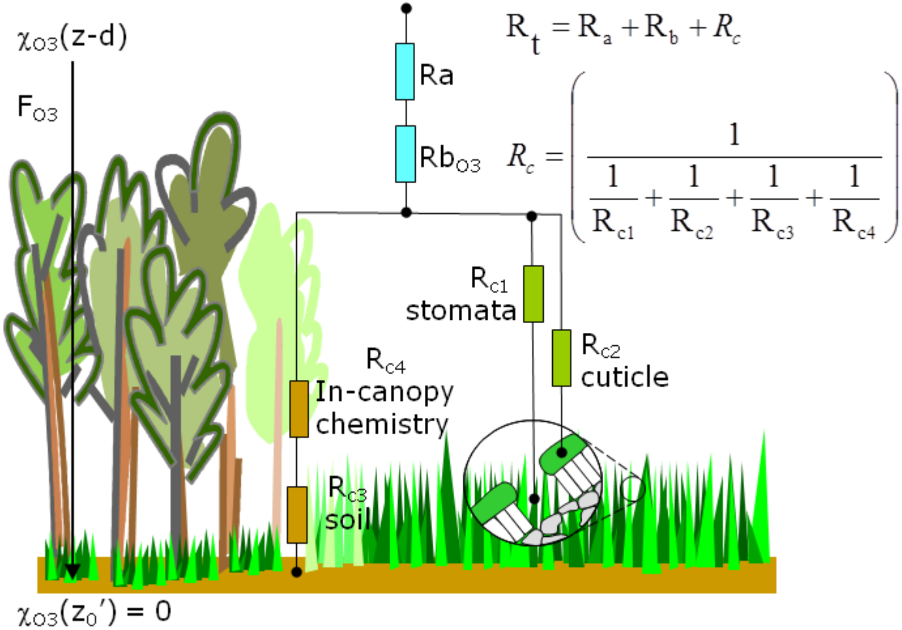

Figure 4. The resistance analogy for ozone deposition to vegetation and soil.

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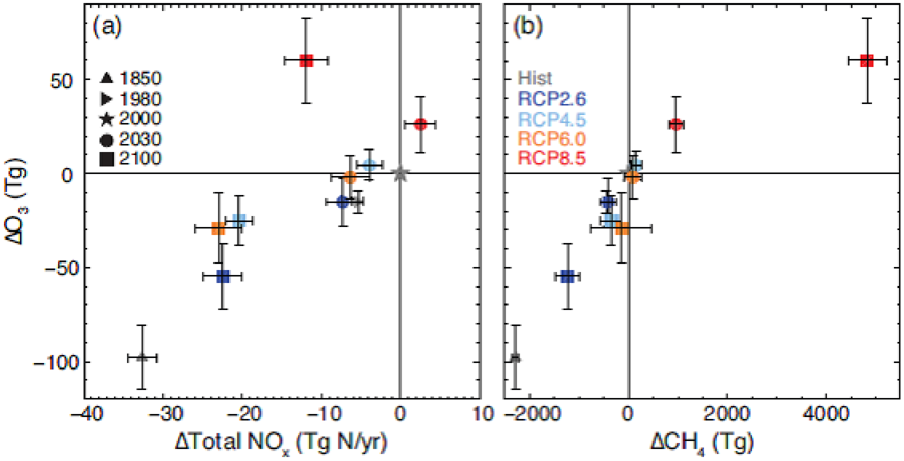

Figure 5. Ensemble mean change in the tropospheric ozone burden compared to the year 2000 simulation as a function of **(a)** changes in total NO_x emissions and **(b)** changes in the tropospheric methane burden. Error bars indicate ±1 SD of the changes in ozone, NO_x emissions and methane burdens, calculated from the spread of the models. Different colours represent the different scenarios, whereas different symbols represent the different time slices (Young et al., 2013).

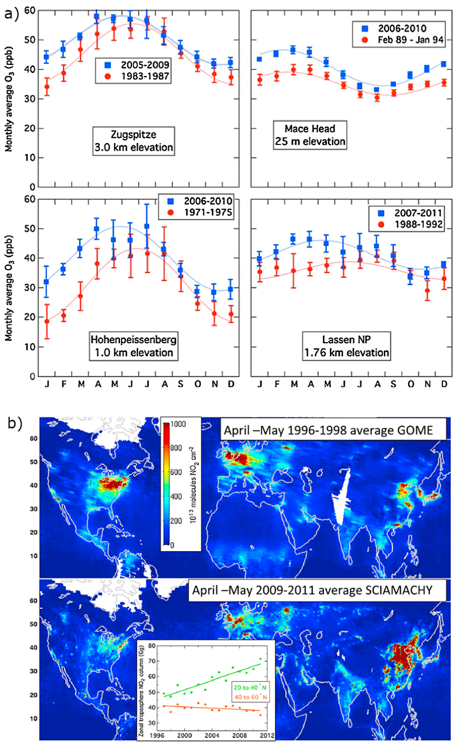

Figure 6. (a) Comparison of O_3 seasonal cycles at three European and one North American site for two periods separated by 17 to 35 years. The data points and error bars indicate 5 year averages and SDs of monthly averaged data for the indicated time periods. The curves of the respective colours are sine function fits to the data. **(b)** Comparison of satellite measured springtime tropospheric NO_2 columns during two time periods separated by 13 years. The inset shows the temporal change in the total zonal troposphere NO_2 column for two Northern Hemisphere Latitude bands (Parrish et al., 2013).

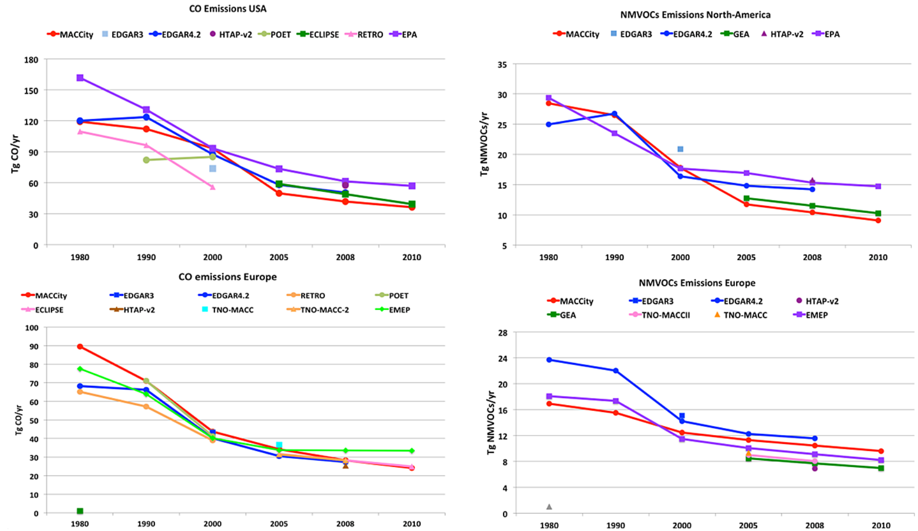

Figure 7. Emissions of CO and NMVOCs in the USA and of NMVOCs in Europe (Western and Central Europe).

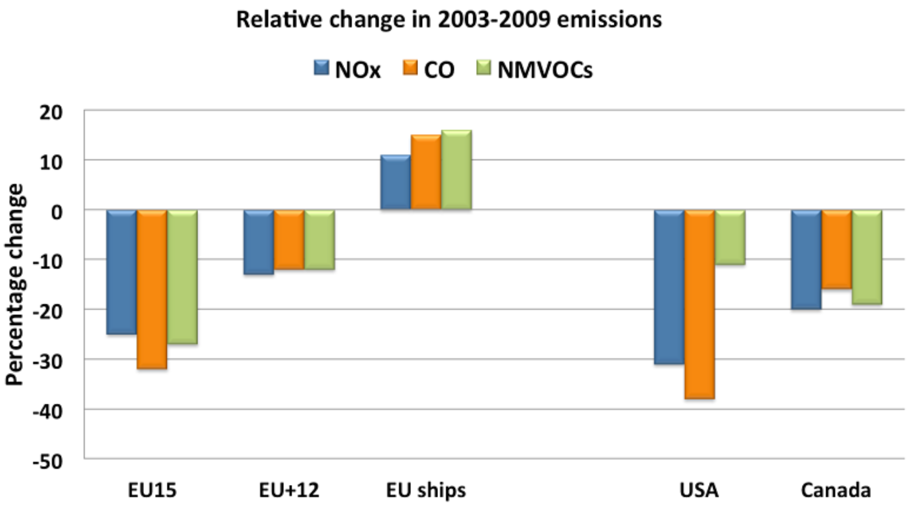

Figure 8. Relative change in NO_x, CO and NMVOCs emissions from 2003 to 2009 (from Kuenen et al., 2014), per country group: EU15 includes the EU Member States in 1995 as well as Norway and Switzerland, EU+12 includes the 12 New Member States, EU ships refers to all European sea regions combined. USA emissions are from the USA Environmental Protection Agency (EPA) and data from Canada are from Environment Canada.

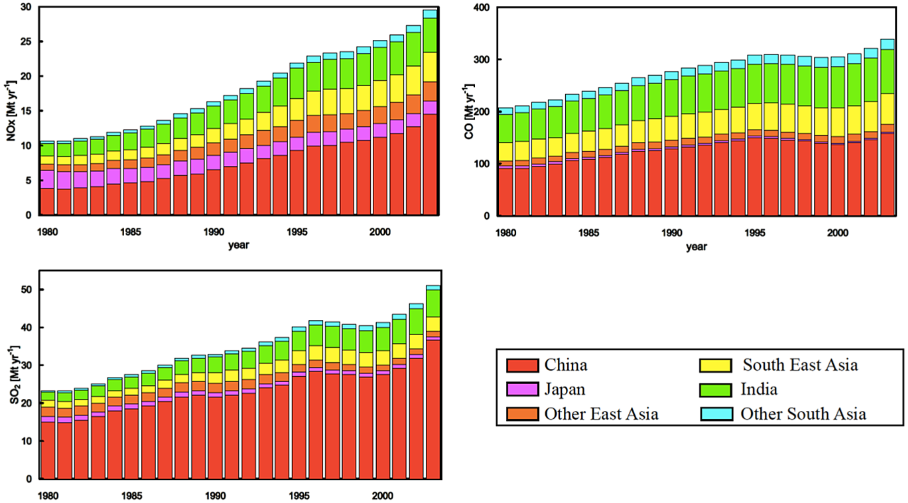

Figure 9. Evolution of surface emissions of CO, NO_x and SO_2 for each Asian region (from Kurokawa et al., 2013).

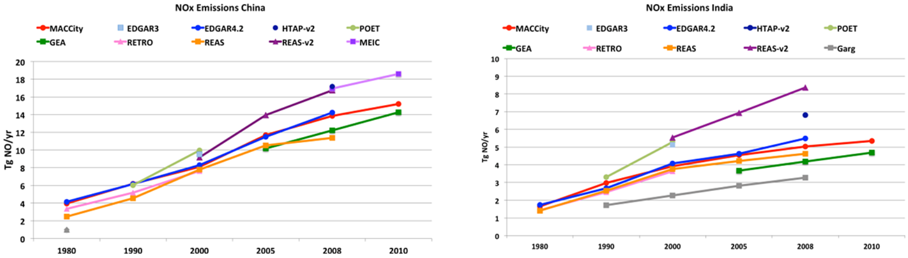

Figure 10. Evolution of NO_x emissions in China and India from 1980 to 2010 provided by different global and regional inventories (units are $Tg\,NO\,year^{-1}$).

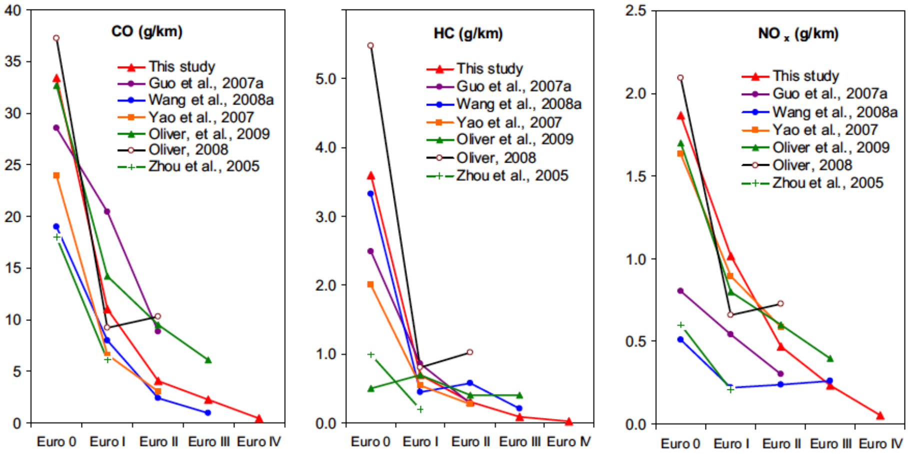

Figure 11. Comparison of emission factors of the LDGVs under real driving conditions from different studies. Note that the emission measurement technologies are different among these studies (from Huo et al., 2012).

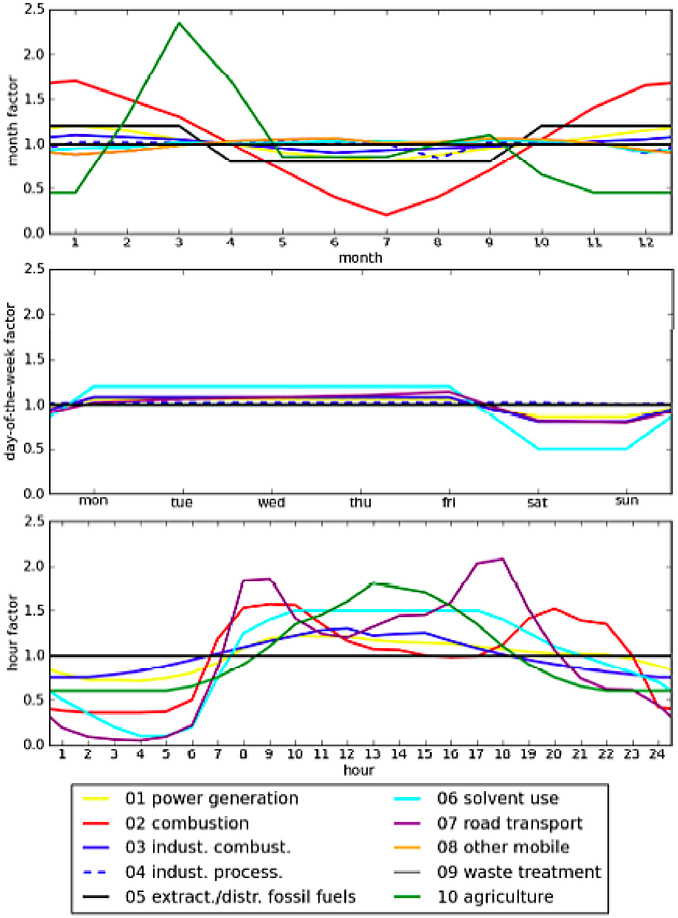

Figure 12. Monthly (top), weekly (middle) and hourly (bottom) time profiles applied to anthropogenic emissions in Europe for different sectors (from Kuenen et al., 2011).

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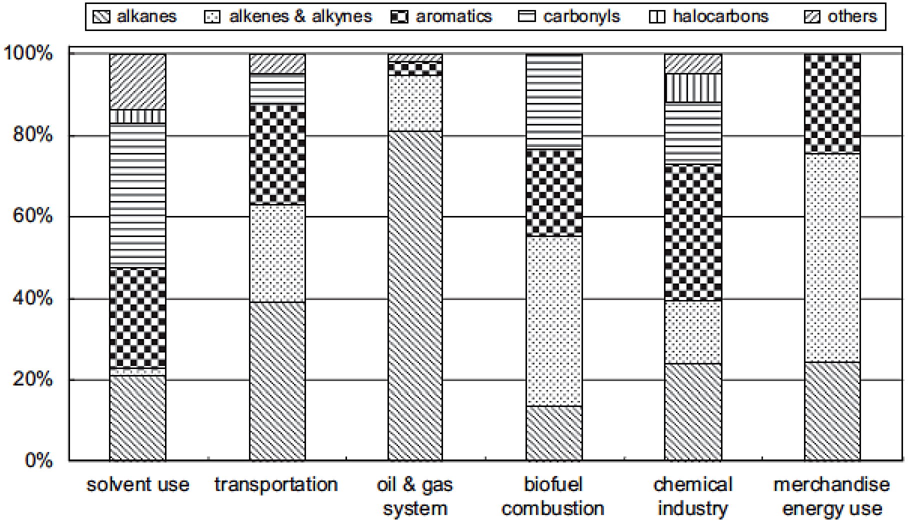

Figure 13. Chemical speciation for various sectors in China (Wei et al., 2008).

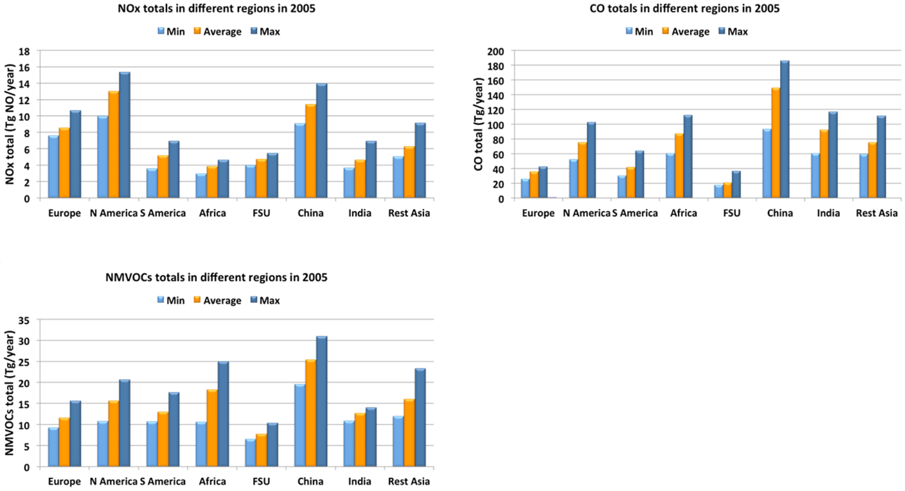

Figure 14. Minimum, average and maximum emissions taken from various inventories of NO_x, CO and NMVOCs for different regions of the world in 2005. The emissions of NO_x are reported in $\mathrm{Tg\,NO\,year^{-1}}$.

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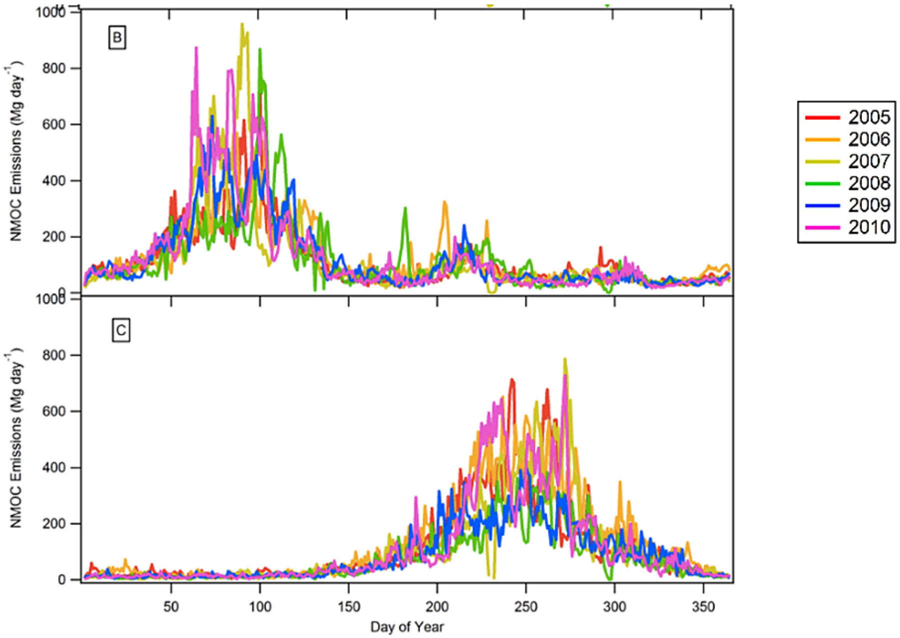

Figure 15. Daily emissions of NMVOC from fires for 2005 through 2010 for the Northern Hemisphere (top) and the Southern Hemisphere (bottom) as represented in the FINN dataset (Wiedinmyer et al., 2011).

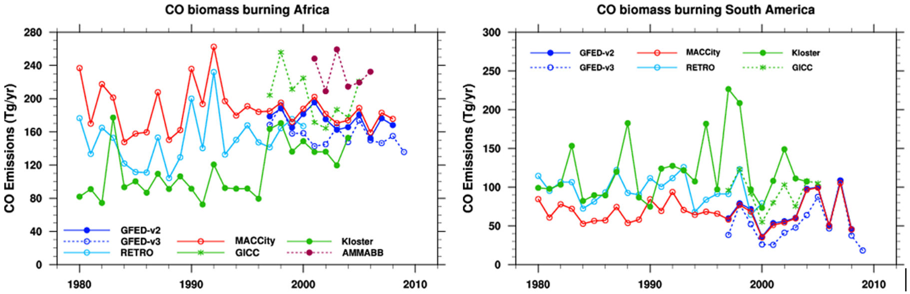

Figure 16. Emissions of CO in Africa (left column) and South America (right column) from 1980 to 2009; from (Granier et al., 2011).

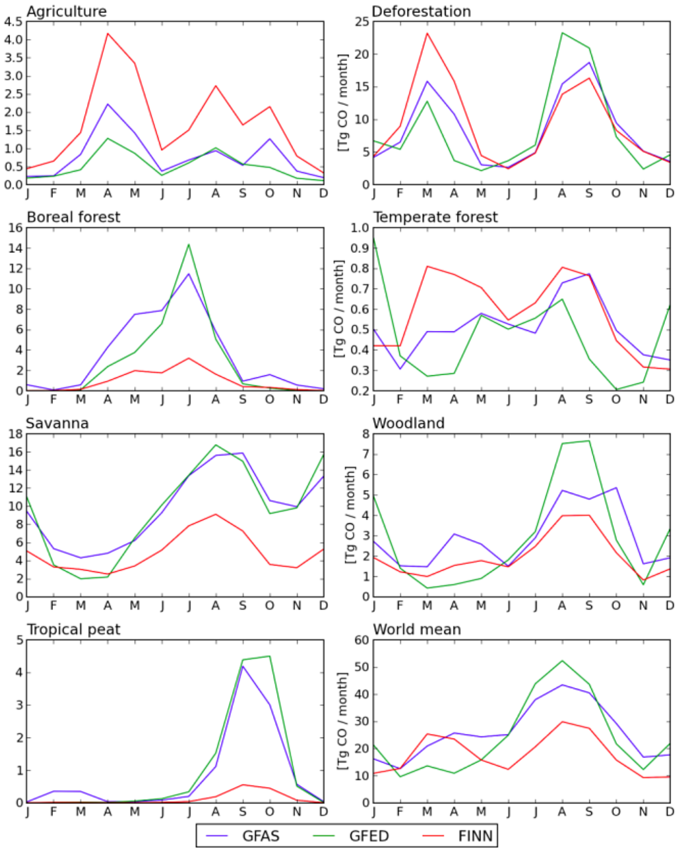

Figure 17. Mean seasonal CO emissions for 7 biomes associated with dominant fire type in GFED (see Fig. 17-1b) and the world for 2003 until 2011. Emissions are shown for three different fire emission inventories: GFAS, GFED and FINN (Kaiser et al., 2013).

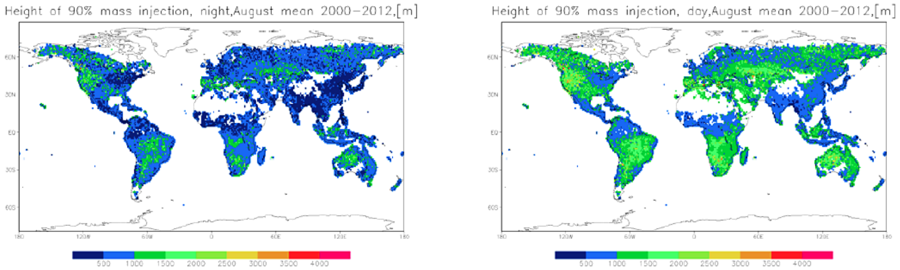

Figure 18. Injection height (in m) for 90 % of mass for night (left) and day (right) for August for biomass burning from (Sofiev et al., 2013).

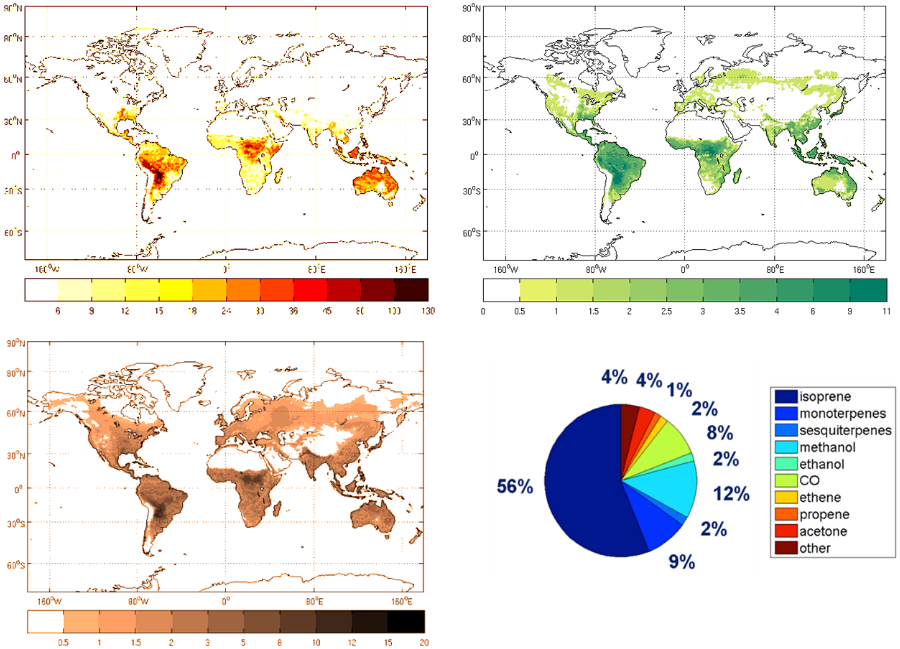

Figure 19. Mean annual emissions (in mg m^{-2} day^{-1}) of isoprene (top left), monoterpenes (top right), methanol (bottom left), and contribution of each BVOCs to the annual global total average (bottom right) (Sindelarova et al., 2014).

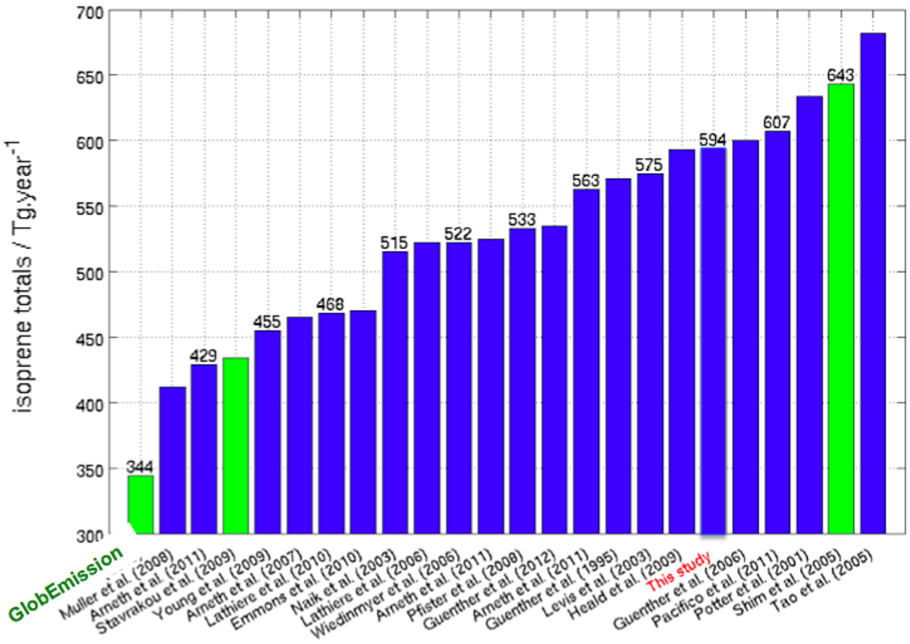

Figure 20. Isoprene global total estimated from different studies. Studies highlighted in green used formaldehyde satellite data and an inversion modeling technique to constrain isoprene emissions (Sindelarova et al., 2014).

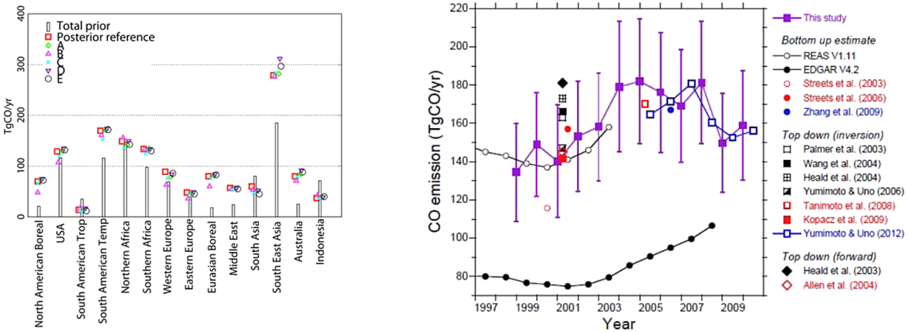

Figure 21. (**a**, left): Annual total posterior CO emissions per region for year 2004 compared to the a priori reference: the different cases correspond to tests on different errors in the model (Fortems-Cheiney et al., 2011). (**b**, right): comparison of estimated CO annual emissions in China from inventories and inverse studies (Tohjima et al., 2014).

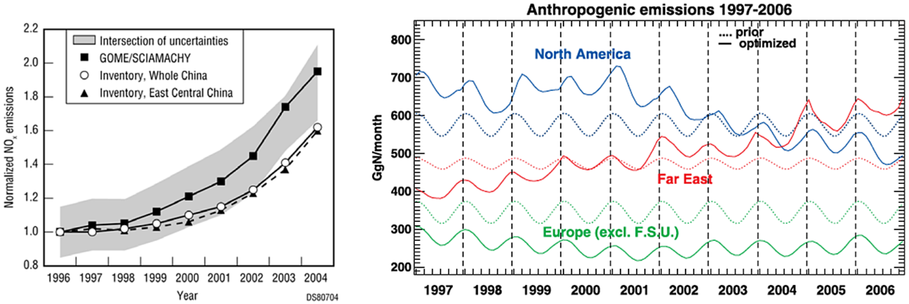

Figure 22. Temporal evolution of NO_x emissions over China from the Zhang et al. (2007) inventory and inverse method using satellite observations. All data are normalized to the year 1996 (Zhang et al., 2007).

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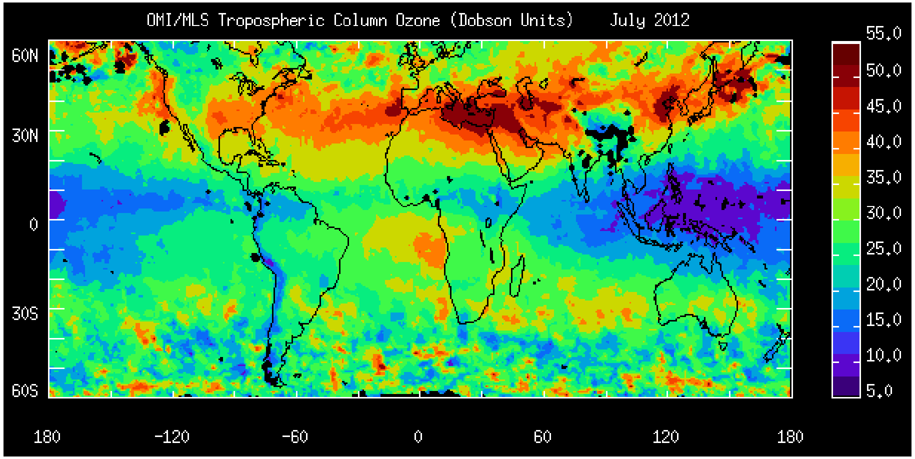

Figure 23. Tropospheric ozone columns determined by residual from OMI observations of total column O_3 and MLS observations of stratospheric O_3 (Ziemke et al., 2006). Plots retrieved from http://acd-ext.gsfc.nasa.gov/Data_services/cloud_slice/index.html#nd.

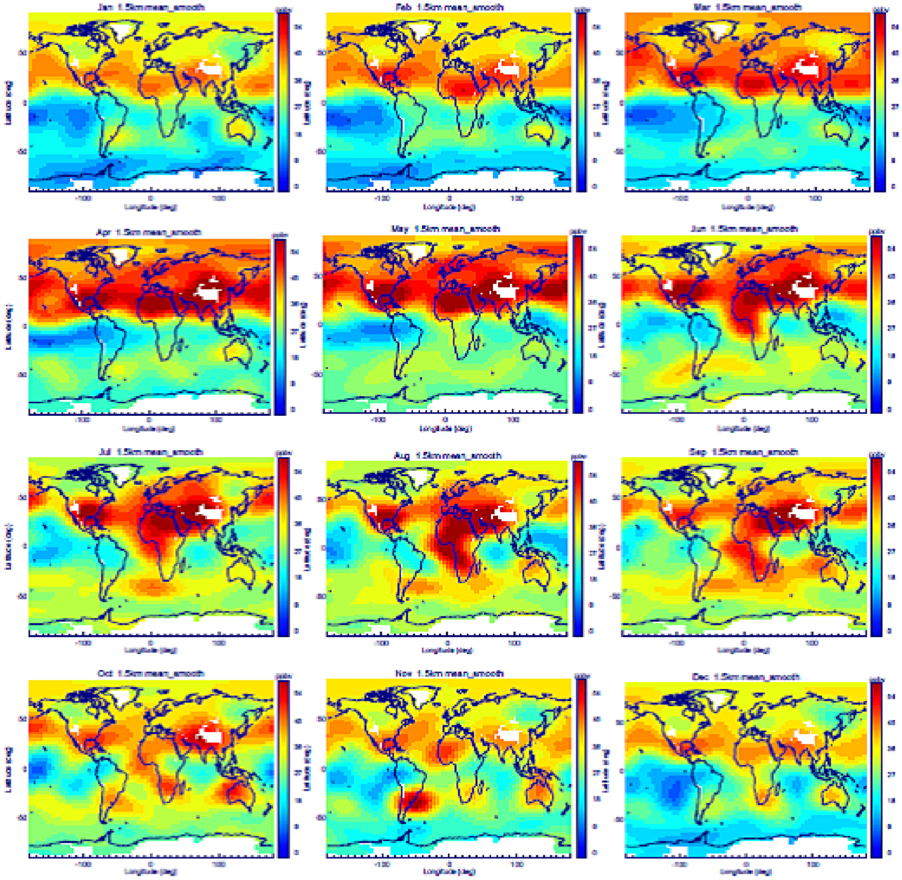

Figure 24. Monthly global ozone distributions at 1.5 km a.s.l. from trajectory mapped ozone soundings (Liu et al., 2013a).

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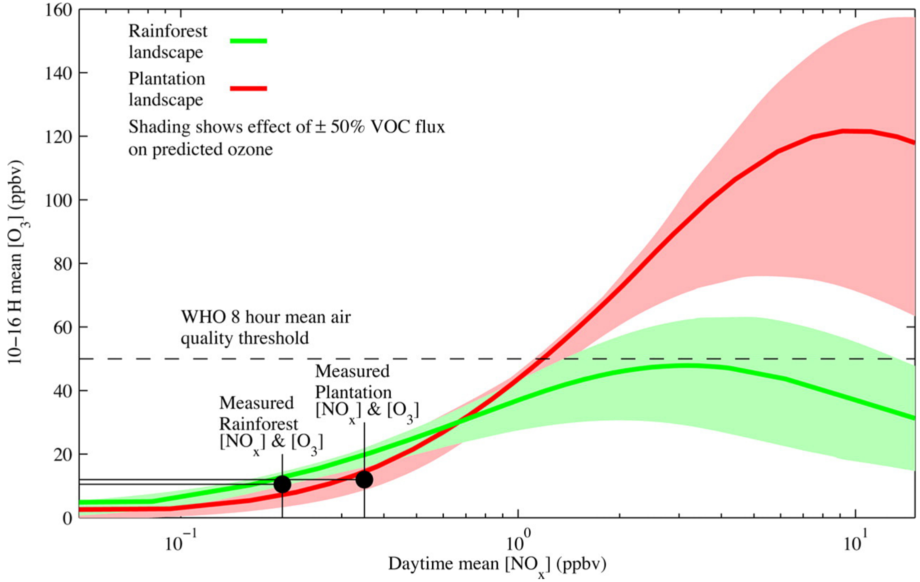

Figure 25. Sensitivity of daytime (10.00–16.00 h) average ozone concentrations to [NO$_x$] in the boundary layer for isoprene and monoterpene emission rates measured in a rainforest and palm oil landscape (Hewitt et al., 2009).

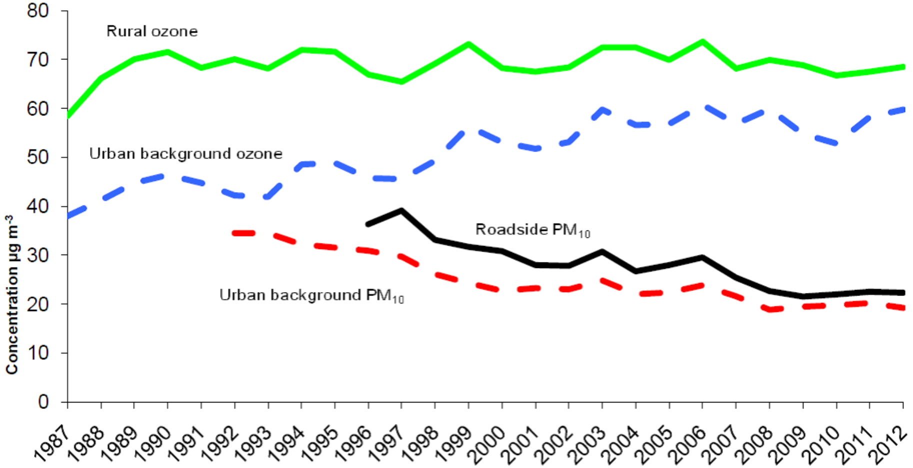

Figure 26. Annual levels of PM$_{10}$ and ozone in the UK 1987–2012 (Defra, 2013).

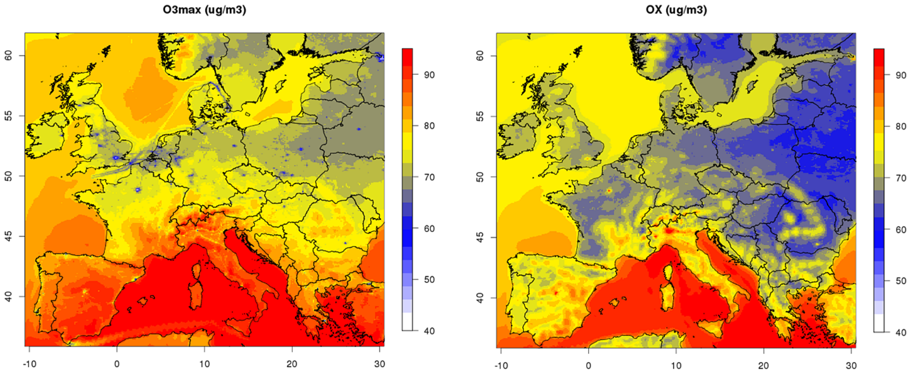

Figure 27. In a continental chemistry transport simulation with the CHIMERE model at a resolution of 8 km, major urban centres in Northern and Central Europe highlight the NO_x titration process (left: summertime average of daily maximum ozone) while the total oxidant level (right: OX as $NO_2 + O_3$, annual mean) is high in most European cities (adapted from Terrenoire et al. (2013), EC4MACS project).

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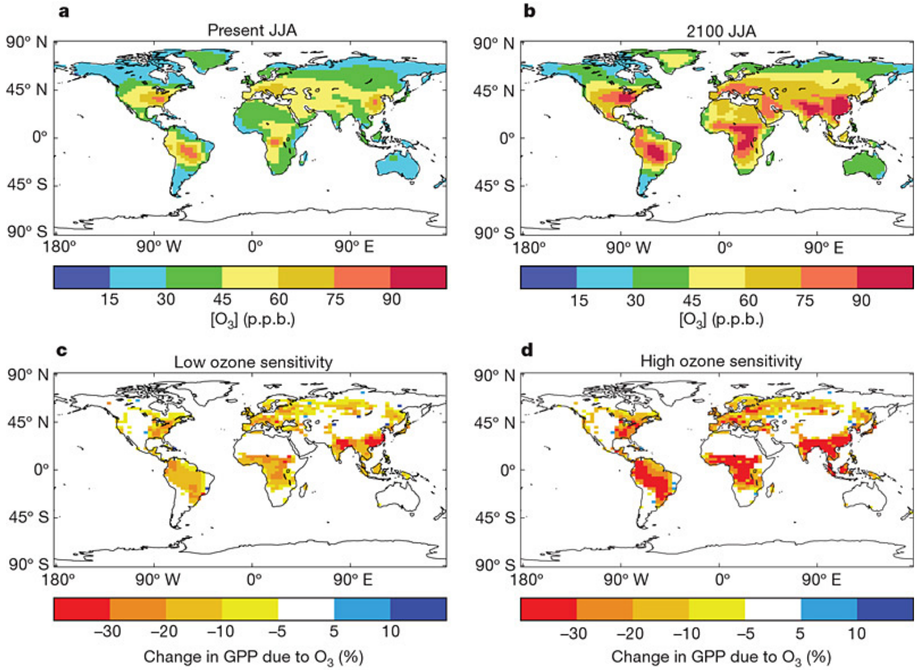


Figure 28. (a, b) Modelled diurnal (24 h) mean surface [O_3] in pbb averaged over June, July and August (JJA) for the present day **(a)** and the year 2100 under the highly polluted SRES A2 emissions scenario **(b)**. **(c, d)** Simulated percentage change in gross primary productivity (GPP) between 1901 and 2100 due to O_3 effects at fixed pre-industrial atmospheric [CO_2] for "low" **(c)** and "high" **(d)** ozone plant sensitivity (Sitch et al., 2007).

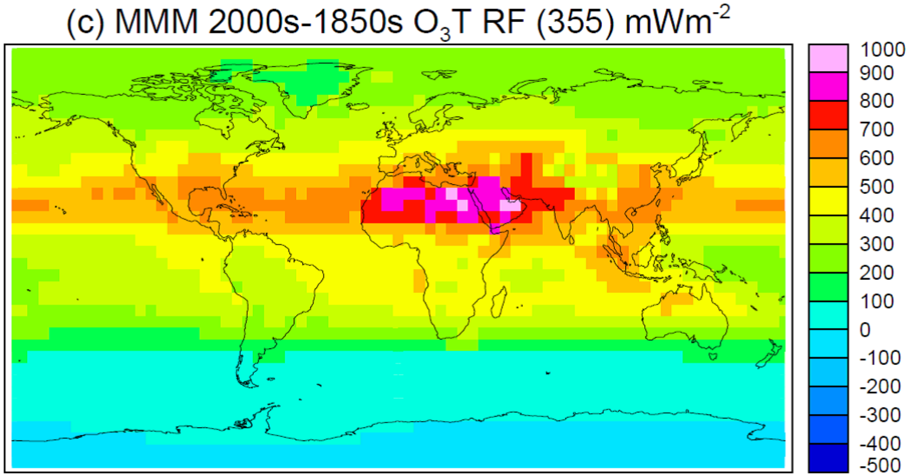


Figure 29. The global distribution of (annual mean) tropospheric ozone radiative forcing (1850–2000, net SW + LW, including stratospheric adjustment, in mW m^{-2}), based on results from the multi-model mean of the ACCMIP models, using the Edwards-Slingo radiation scheme (Stevenson et al., 2013). (NB the value of 0.355 W m^{-2} shown here compares to the recommended IPCC value for the 1750–2010 O3 RF of 0.40 W m^{-2}; the IPCC value includes the additional time periods 1750–1850 and 2000–2010, and also incorporates calculations with additional radiation schemes, and from other studies.)

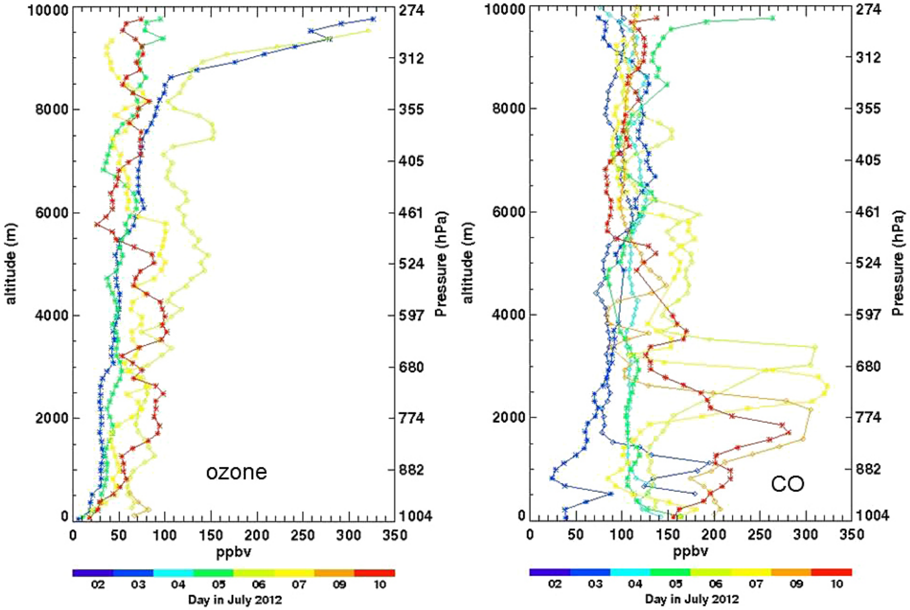


Figure 30. Ozone and carbon monoxide vertical profiles over Vancouver recorded by IAGOS (http://www.iagos.org/) in July 2012 (courtesy of Hannah Clark).

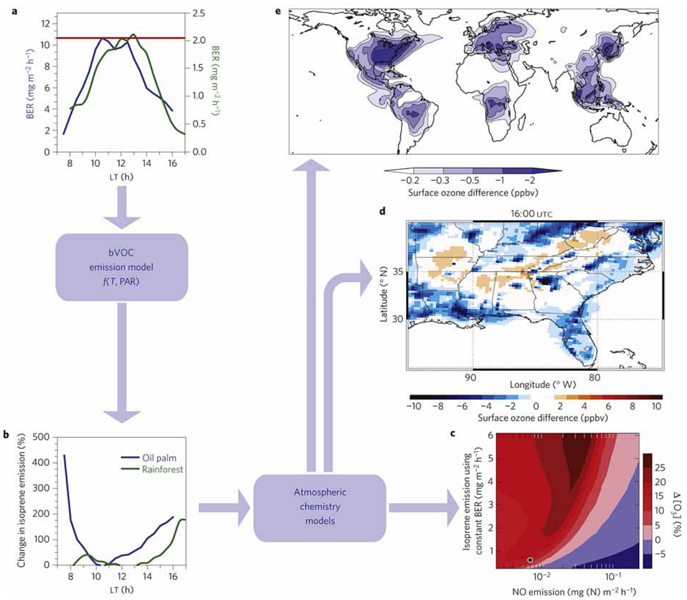


Figure 31. The effect of a circadian rhythm based biogenic emission rate (BER) on ozone; **(a)** the oil palm plantation (blue) and rainforest (green) BERs of isoprene compared with a constant BER (red). **(b)** The differences in isoprene emission rates between constant (red line in **(a)**) and circadian-controlled BERs (oil palm: blue; rainforest: green); **(c)** changes in ground-level ozone resulting from changing isoprene and nitrogen oxide emission rates. **(d)** Changes in regional-scale modelled ground-level ozone for 11:00 LT using an "oil palm" circadian-controlled BER compared with a constant BER. **(e)** Changes in global-scale modelled ground-level ozone for July using the same scenario as **(d)** (Hewitt et al., 2011).

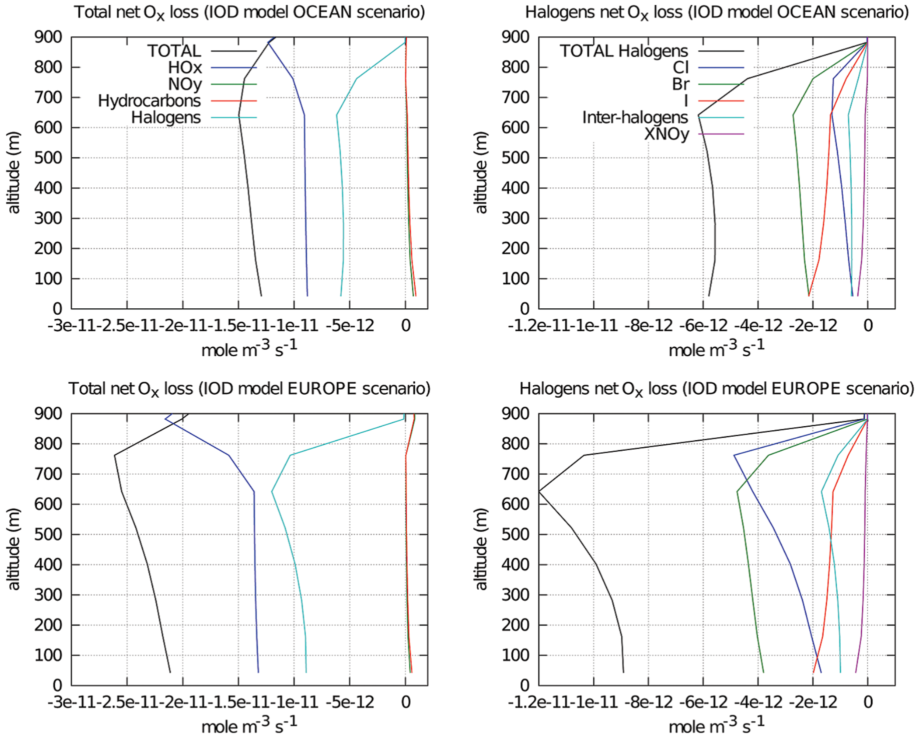
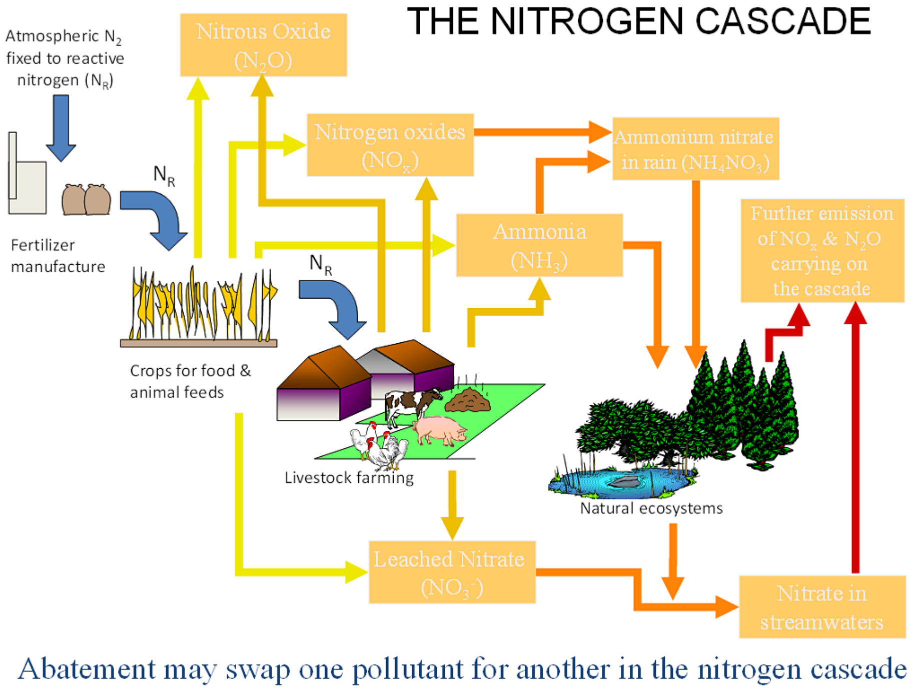


Figure 32. Vertical profiles at 12:00 LT of total and halogens net O_x loss in unpolluted (OCEAN scenario) and semi-polluted (EUROPE scenario) marine boundary layer (Sommariva and von Glasow, 2012).



Abatement may swap one pollutant for another in the nitrogen cascade

Figure 33. The nitrogen cascade adapted from Sutton et al. (2011).

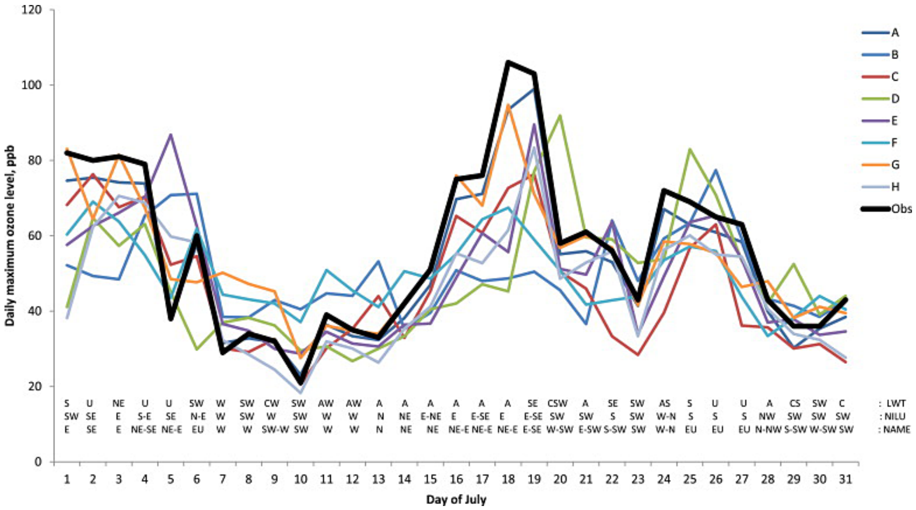


Figure 34. Daily maximum hourly ozone concentrations for eight models A–H in a comparison exercise against observations for July 2006 at Harwell, Oxfordshire, UK. Also shown are the daily advection regimes as Lamb Weather types (LWT), NILU FLEXTRA trajectories (NILU) and NAME air history maps (NAME), see Derwent et al. (2014).

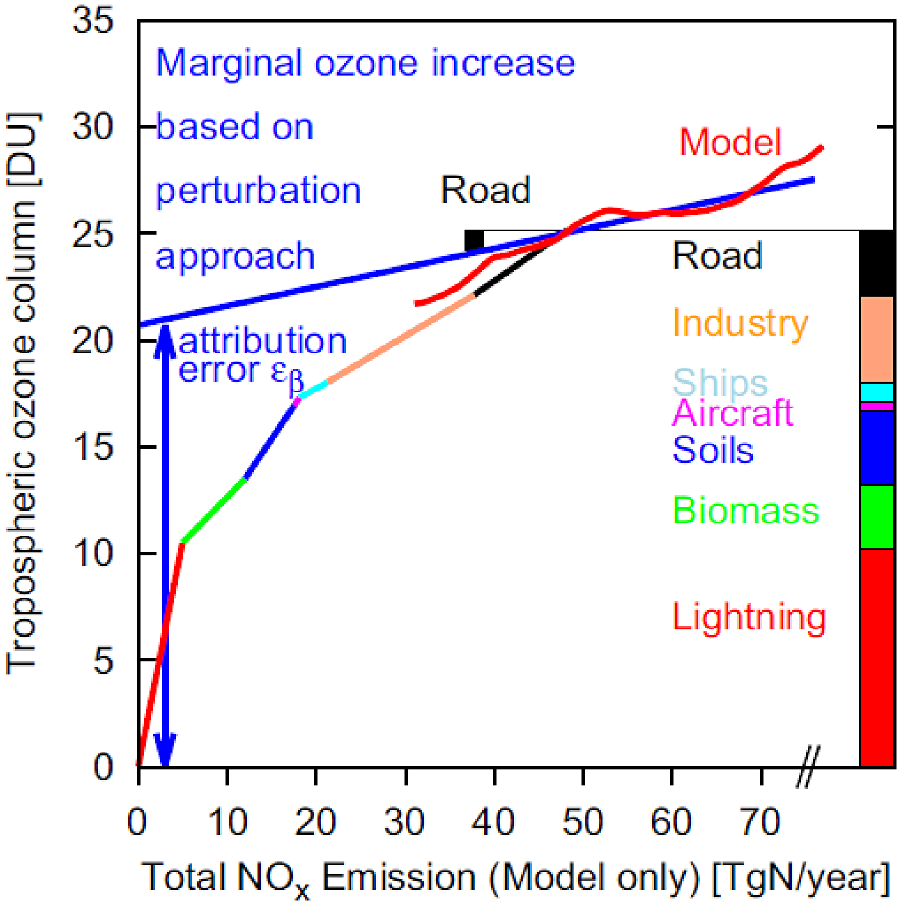


Figure 35. Contribution of individual sectors in terms of NO$_x$ emissions to the tropospheric ozone column (Grewe et al., 2012).

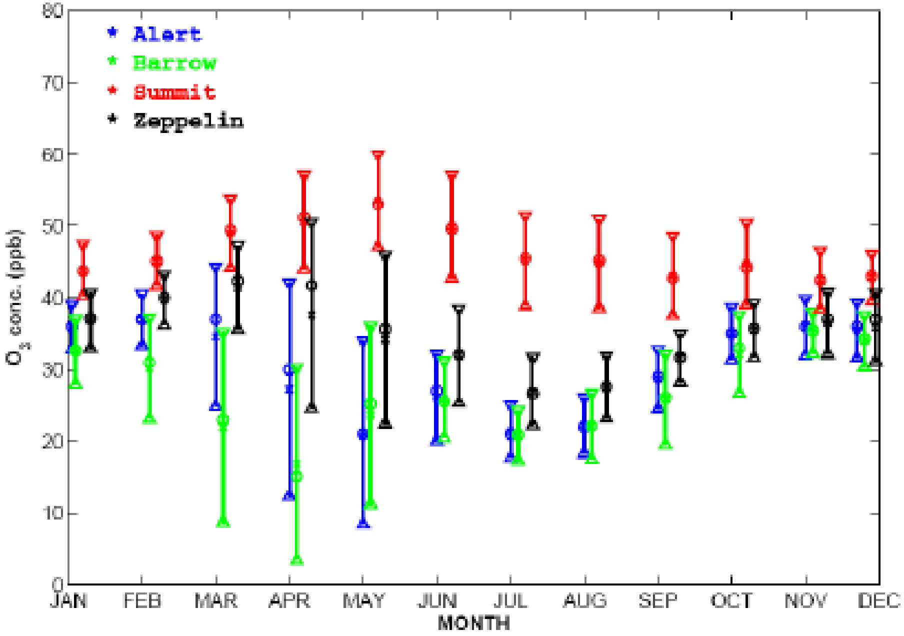


Figure 36. Seasonal cycle of O_3 at various surface sites in the Arctic. From Hirdman et al. (2010).

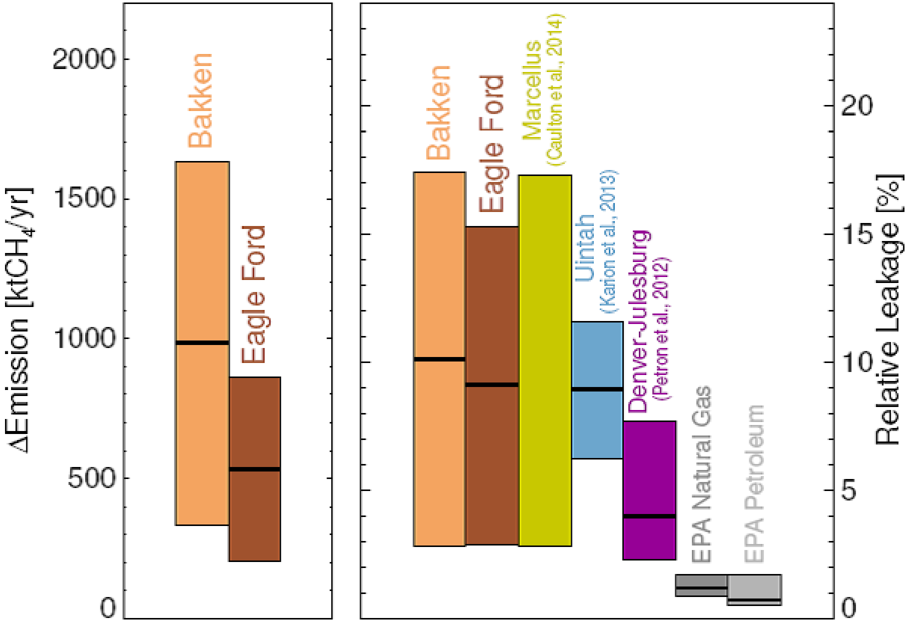


Figure 37. Estimated methane emissions are shown for the targeted regions Bakken in light brown, and Eagle Ford in dark brown from satellite remote sensing measurements (Schneising et al., 2014). Shown are absolute emission increase (2009–2011 relative to 2006–2008) in the left panel, and the leakage rate relative to production in the right panel, with the 1σ uncertainty ranges. For comparison, leakage estimates from previous studies in Marcellus (2012) (Caulton et al., 2014), Uintah (2012) (Karion et al., 2013), Denver-Julesburg (2008) (Pétron et al., 2012). EPA bottom-up inventory estimates for natural gas and petroleum systems (2011) are shown for comparison (EPA, 2014).

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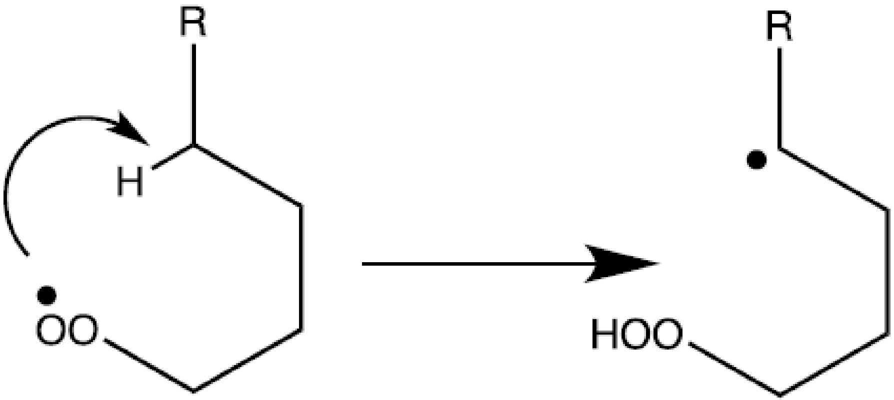

Figure 38. RO_2 isomerisation to QOOH. In this mechanism, well known in combustion chemistry, the terminal O atom of the RO_2 abstracts a labile H (through the formation of a ring structured intermediate).

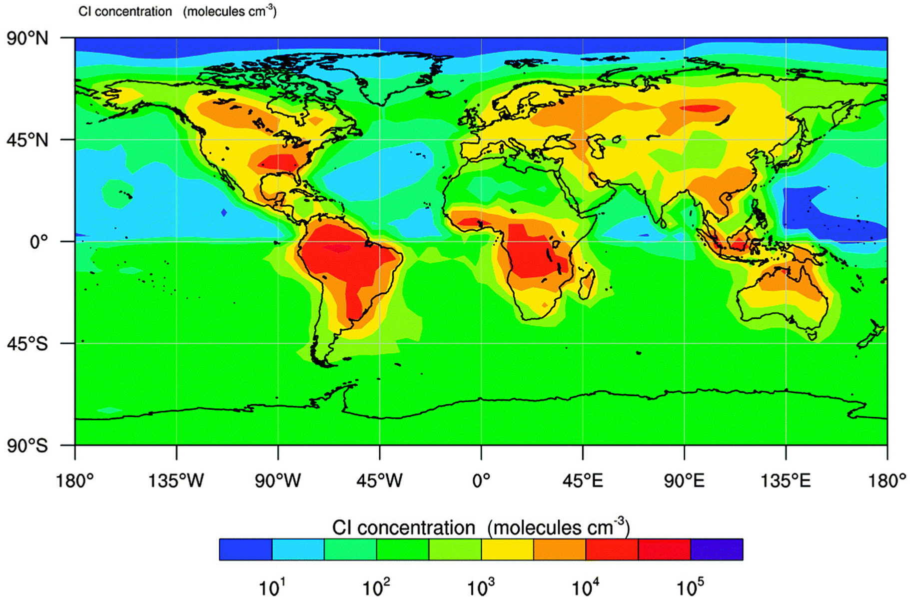

Figure 39. Global surface averages model concentrations of the Criegee Intermediate concentration (Taatjes et al., 2014).

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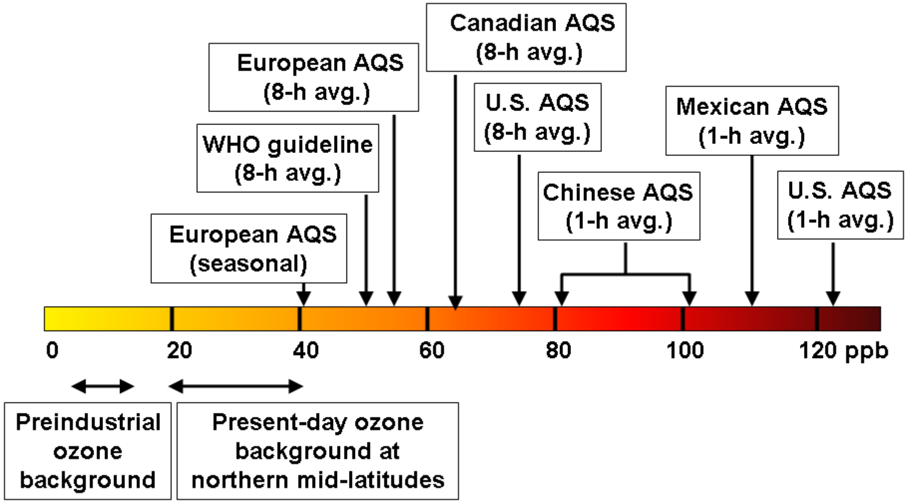

Figure 40. Ozone Air Quality Standards (AQS) in ppb. Different national and international standards are noted as well as estimates for northern midlatitudes of the preindustrial background (i.e., O_3 abundances with all anthropogenic emissions of NO_x, CO, VOC, and CH_4 switched off, and before current climate and stratospheric O_3 change) and the present-day baseline abundances (i.e., the statistically defined lowest abundances of O_3 in air flowing into the continents, typical of clean-air, remote marine sites) from (Council, 2009a).

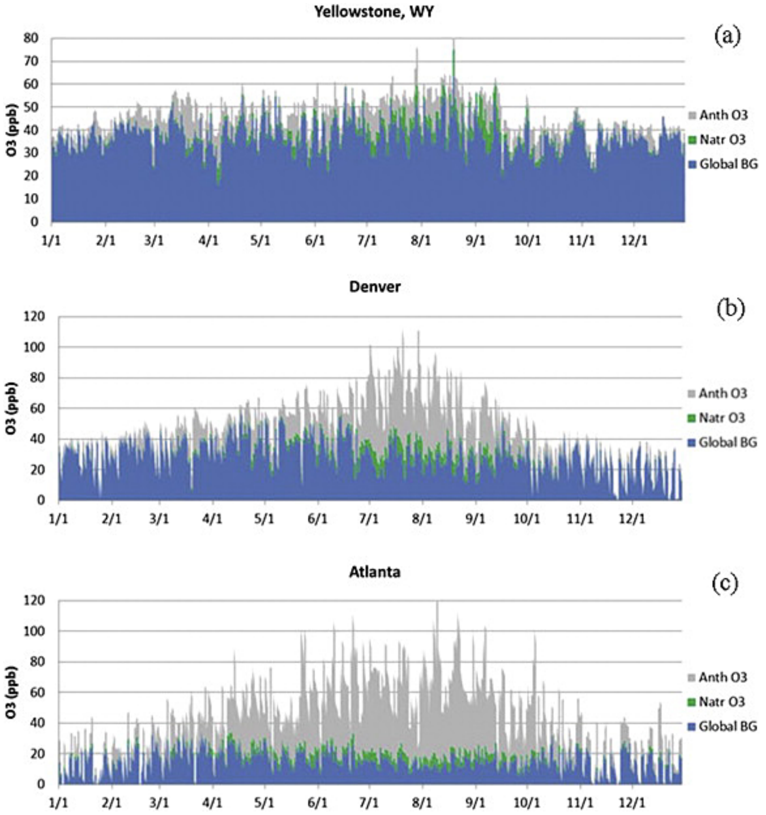

Figure 41. Modeled contributions of hourly GBO_3 (global tropospheric O_3 plus stratospheric O_3), natural (Natr O_3), and anthropogenic (Anth O_3) adding to total hourly O_3 for **(a)** Yellowstone NP, **(b)** Denver and **(c)** Atlanta (Lefohn et al., 2014).

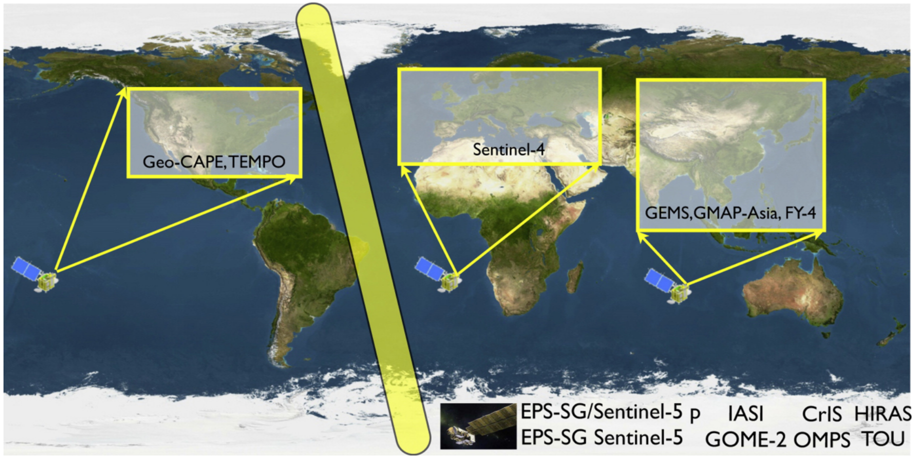

Figure 42. Constellation of geostationary and low-earth orbiting satellites planned for the coming decade that will measure tropospheric ozone. Current instruments that measure tropospheric ozone, e.g., TES or OMI, but will not be continued in the future are not listed, Bowman (2013).

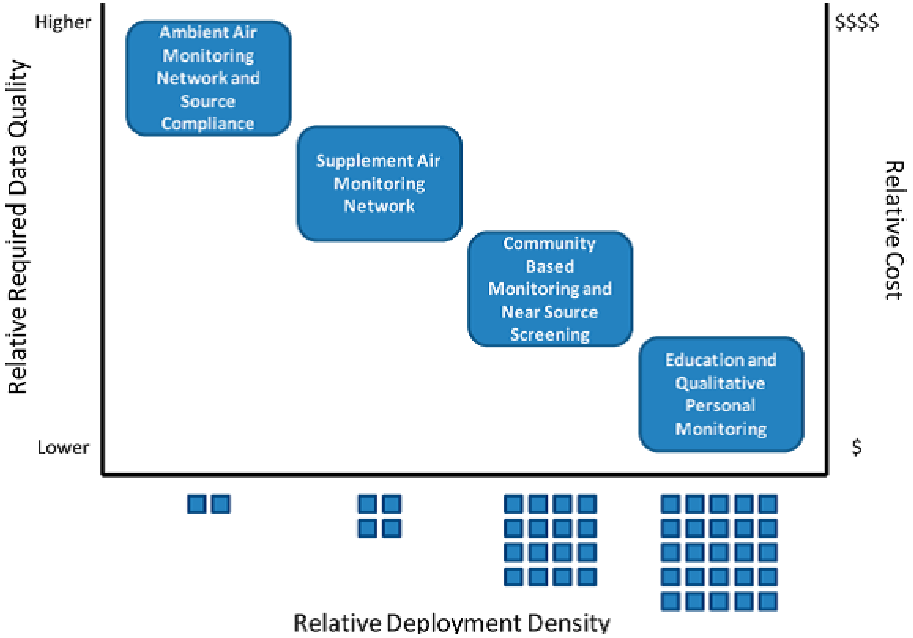

Figure 43. Relative data, quality, cost and deployment density for small sensor networks for air quality (Snyder et al., 2013).